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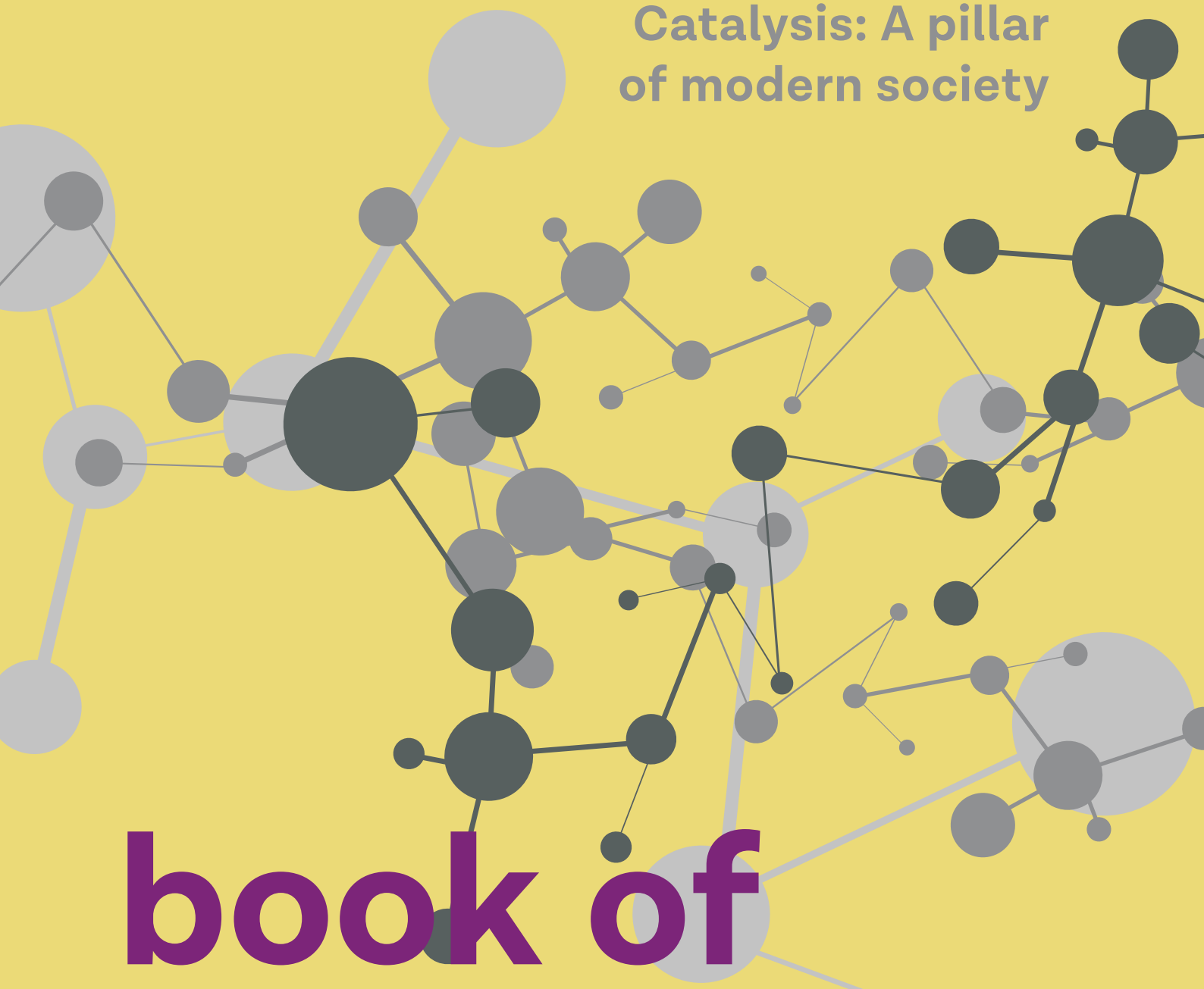

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Plenary lectures

Birth, life and aging of heterogeneous catalysts seen by the eye of a spectroscopist.

Silvia Bordiga

Department of Chemistry, NIS Center and INSTM Reference Center, University of Turin, Via Quarello 15, 10135, Turin, Italy.

By definition, in a reaction what is acting as a catalyst is not consumed and remain unchanged after it. However it is a commune experience to handle with birth, life and aging of our catalysts. For this reason it is crucial to be able to characterize, at the best level we can, birth, life and aging evolution of our catalysts, in order to get structure-properties correspondance aiming to improove catalysts preformances.

In this context, a selection of case studies involving zeolites as catalysts, will be illustrated showing the complementar roles of some spectroscopic techniques used in situ or following operando conditions, underlying their pros and cons.

Acknowledgments

Silvia Bordiga is deeply in debt with all the past and present colleagues and students that along the last 33 years have contributed to develop the research illustrated in the contribution.

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Frontiers in Olefin Metathesis: Toward the Realization of a Nobel Promise

Deryn E. Fogg

Centre for Catalysis Research & Innovation, and Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Canada K1N 6N5 and Department of Chemistry, University of Bergen, Bergen, Norway

Olefin metathesis is an exceptionally versatile methodology for the catalytic assembly of carbon-carbon bonds. Long embraced by synthetic chemists in discovery operations in academia and industry, molecular metathesis catalysts are now beginning to see uptake in pharmaceutical manufacturing (Figure 1a).[1] This is a welcome development, as they have tremendous potential to reduce the environmental footprint associated with production of active pharmaceutical ingredients. However, this and other demanding contexts (in particular chemical biology) reveal major limitations arising from short catalyst lifetimes.

The pathways by which the important ruthenium catalysts deactivate or decompose are now coming into focus. We believe that such understanding is key to designing better processes and, ultimately, better catalysts. Insights will be described into the operation and decomposition of key metathesis catalysts, including the most recent generation of high-performing cyclic alkyl amino carbene catalysts (CAAC; Figure 1b). These will be tied to key challenges and new opportunities relating to catalyst design, synthesis, and deployment. More broadly, these studies highlight the importance of advancing the critically important science of catalysis decomposition, a little-explored frontier in molecular catalysis.

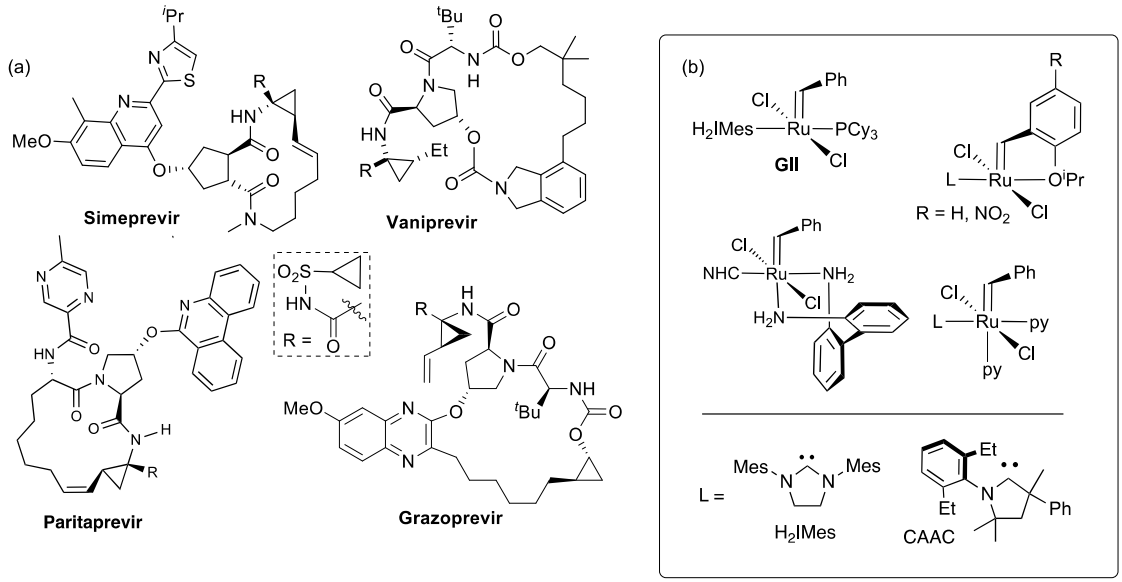

Figure 1. (a) Antiviral Drugs Accessible via Ring-Closing Metathesis. (b) Key Metathesis Catalysts.

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Towards understanding catalysis at water-solid interfaces

Johannes A. Lercher

Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, WA
Department of Chemistry Technische Universität München, Garching, Germany

The radical changes necessary for transitioning towards a future energy and chemical industry that achieves carbon neutrality demand reconsideration of catalytic conversions under conditions previously deemed challenging. A crucial aspect involves adopting environmentally benign solvents and diluents such as water or biogenic solvents. The modifications induced by these solvents create obstacles for catalyst performance and stability, yet they also unveil new opportunities to leverage the induced excess chemical potentials of reactive substrates.

Water, along with other polar molecules, self-organizes on oxide catalyst surfaces and within microporous materials. Their presence and self-organization affect sorption and catalysis by modifying the chemical and thermodynamic properties of both the solid environment and the hosted molecules. Water forms well-structured hydrated hydronium ions at Brønsted acid sites in micropores of all dimensions. The sizes of these clusters depend on the environment and are constrained by the entropy loss relative to condensation outside the micropores. Notably, the remaining pore space is predominantly vacant in the exclusive presence of water. This inhomogeneity is not the consequence of weak interactions between the zeolite pore wall and water, but caused by the internal stabilization of the hydrate clusters.

Other molecules are adsorbed in the space among hydronium clusters, and small polar molecules may partially substitute for water in the cluster, either forming the hydrated hydronium ion or clustering around metal cations. The concentration and thermodynamic state of adsorbed and reacting molecules are influenced by the characteristics of the interacting sites, the steric environment, and the density of charged species. This complex environment leads to a pronounced (de)stabilization of both ground and transition states, thereby both augmenting and impeding the rates of catalytic pathways. This results in a maximum of catalytic activity with increasing charge density, a phenomenon absent on open surfaces and associated with the energy required to reorganize charges within the confined spaces of narrow pores.

Water layers on metal particles on the other hand induce changes by influencing the electronic surface properties and influencing binding of hydrogen on these metal surfaces. In turn, the strength of this binding determines rates of hydrogen addition reactions. Changing the binding of hydrogen by external electric potentials opens additional new pathways to enhance these reactions and also facilitates pathways involving coupled transfer of H^+ and electrons.

For both acid-base and metal catalyzed reactions, the lecture will show the links between these underlying physicochemical causes for the observed changes induced by water in sorption and catalysis and will discuss opportunities and limitations for developing new catalytic pathways for a circular carbon-neutral catalysis.

Catalysis using gold containing materials

Graham J. Hutchings*

Max Planck Centre for the Fundamentals of Heterogeneous Catalysis, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK
**hutch@cf.ac.uk*

Keywords: gold, palladium, oxidation, hydrogenation.

Catalysis is of crucial importance for the manufacture of the goods and infrastructure and underpins the manufacture of most goods. Hence designing new catalysts is a topic of intense research interest in the scientific community. The identification that gold in nanoparticulate or cationic form is an exceptionally effective catalyst has paved the way for a new class of active catalysts. Gold is the most active catalyst for CO oxidation and acetylene hydrochlorination and recent research on this will be described. In particular, the innovations that were required to enable the commercialization of a gold catalyst will be described. Alloying gold with palladium can enhance the activity for alcohol oxidation as well as the direct synthesis of hydrogen peroxide. However, most recently it has been found that spatial separation of Au and Pd nanoparticles on a conducting support can give a significantly enhanced activity for alcohol oxidation via a novel cooperative enhancement effect (CORE). In this lecture the following topics will be covered:

Part 1 Gold Catalysis

- Carbon Monoxide oxidation[1]
- Acetylene hydrochlorination[2,3]
- Methane oxidation[4]

Part 2 Gold Palladium Catalysis

- Alcohol oxidation,[5,6]
- Direct H_2O_2 synthesis[7] and use of in situ generated H_2O_2 for coupled reactions[8,9]

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Identification of Solids for True Design and Precise Characterization of Functional Materials

Bunsho Ohtani

Professor Emeritus, Hokkaido University and Nonprofitable Organization touche NPO, Sapporo,Japan
bunshoohtani@gmail.com

Keywords: electron trap, idenfication of solid materials, reversed double-beam photoacoustic spectroscopy

Introduction. How can we design functional solid materials, such as catalysts and photocatalysts? What is the decisive structural parameters controlling their activities, performance or properties? What is obtained as structural properties by popular conventional analytical methods, such as X-ray diffraction (XRD) or nitrogen-adsorption measurement, is limited to bulk crystalline structure and specific surface area, i.e., no structural characterization on amorphous phases, if present, and surface structure has been made so far. This is because there have been no macroscopic analytical methods to give surface structural information including possibly-present amorphous phases. Recently, we have developed reversed double-beam photoacoustic spectroscopy (RDB-PAS) which enables measure energy-resolved distribution of electron traps (ERDT) for semiconducting materials such as metal oxides [1,2].

Experimental/methodology. ERDT patterns were measured by RDB-PAS as reproted previously [1,2]. Brief description of the method is excitation of electrons in the valence band of semiconducting samples are excited to electron traps by wavelength-scanned (from longer to shorter) monochromatic continuous light to give photoabsorption followed by detection by photoacoustic (PA) spectroscopy using intensity-modulated LED-light beam. ERDT patterns were obtained by differentiation of the PA intesity trace and calibration to absolute value in the unit of μmol g^{-1}. Conduction-band bottom (CBB) energy was calculated from photoabsorption-edge wavelength maasured by conventional PA spectroscopy and shown in reference to valence-band top (VBT) energy in the unit of eV.

Results and discussion. For almost all the metal oxide samples, suchi as titania, in powder form, the detected electron traps (ETs) seem to be predominantly located on the surface, and therefore they reflect macroscopic surface structure, including amorphous phases. On the other hand CBB might reflect bulk structure of samples. Even if the bulk structure suggested by CBB and surface area suggested by total density (TD) of ETs are similar, different samples showed different ERDT patterns suggesting that the surface structure of samples are different among the samples of similar particle size and bulk structure. Therefore, it can be said that RDB-PAS is sole possible methodology for macroscopic detection of the surface structure of solids. Another significan point is that the activity, performance or the other properties of two samples showing resembling ERDT/CBB patterns is almost identical with each other, i.e., those samples are "identified" by ERDT/CBB patterns. As far as the author knows, this is the first result for identification of solids. In this talk, an approach of "true" material design based on the ERDT/CBB-pattern analyses is introduced [3,4].

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Catalysis and Sustainability: A Journey from Atom to Planet

Javier Pérez-Ramírez

Institute for Chemical and Bioengineering, ETH Zurich, Switzerland
jpr@chem.ethz.ch

Ensuring a sustainable future for the chemicals and energy industries is a pressing global concern that has far-reaching impacts on the environment, human health, quality of life, and the economy. Catalysis plays a crucial role in this journey, constantly pushing the boundaries of conventional design to spearhead the transition towards defossilized and circular chemical manufacturing. This talk aims to illustrate the interdisciplinary and cross-scale mindset required to design catalysts that meet the ever-evolving sustainability criteria, bridging the gap between atom and planet. Delving into the latest research from my laboratory, I will showcase how a deeper understanding of catalyzed processes is driving revolutionary technological advancements. Through case studies in key areas such as CO_2 valorization, polymer manufacture, and organic synthesis, I will exemplify how nanoscale engineering and the availability of increasingly powerful tools to access structural variations and mechanism under relevant conditions aid catalyst discovery. At the forefront of design, I will demonstrate the importance of precisely controlling the architecture, speciation, and dynamics of supported metals in low-nuclearity catalysts, highlighting the impact that even the smallest changes can have on performance. The presentation will touch on current frontiers in catalyst synthesis and characterization, and emphasize the critical role of quantitative metrics in guiding low-carbon strategies.

Molecular understanding of multifunctional electrocatalysts for water and hydrogen oxidation

Xile Hu *
Ecole Polytechnique Fédérale de Lausanne (EPFL), Institute of Chemical Sciences and Engineering, EPFL-ISIC-LSCI, BCH 3305, Lausanne, CH 1015, Switzerland
* *xile.hu@epfl.ch*

Abstract. The development of efficient and Earth-abundant water and hydrogen oxidation catalysts is essential for the generation and use of renewable hydrogen. Real-life catalysts are typically multicomponent, with each component contributing to one or more functions. The fundamental understanding of these catalysts is still lacking, which makes the rational design of catalysts difficult. In this talk, I will first present our work in understanding nickel iron oxyhyoxides, the current benchmark catalyst for water oxidation. We use multiple operando spectroscopy, electrokinetics, and isotope labelling experiments to elduciate the active sites and mechanisms of this catalyst.[1-2] Then I will show our discovery of a novel iron nickel oxide catalysts that surpress the performance limit of conventional nickel iron oxyhydroxides, due to its cooperative mechanism.[3-4] This catalyst has found application in cutting-edge anion exchange membrane water electrolyzers (AEMWEs). In the second part I will present our work in developing hydrogen oxidation catalysts for anion exchange membrane fuel cells (AEMFCs). I will show how we achieve a low-pltatinum-group-metal AEMFCs by using a porous support to tune the electronic properties of PGM nanoparticles.[5] Then I will describe our work in developing non-PGM catalysts for hydrogen oxidation. In particular I will highlight a catalyst made of Ni nanoparticles supported on a nitrogen-doped carbon. The electronic interaction between the Ni nanoparticles and its support leads to balanced hydrogen and hydroxide binding energies, which resulted in the highest (electrochemical surface area-normalized) intrinsic activity for PGM-free catalysts.[6] This catalyst has been used in HEMFC, delivering a peak power density that is more than 6 times higher than previously best devices.

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Follow the format below for this purpose:

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Keynote lectures

Renewable fuel from waste in the circular economy era

Carlo Perego

Senior Advisor, Italy
E-mail address (caregoperlo54@gmail.com)

Keywords: renewable fuels; advanced biofuels, biomass waste; biochemical processes; thermochemical processes.

Transition to carbon neutrality requires drastic changes to happen as summarized by the International Energy Agency in "Net Zero by 2050" report, which defines a roadmap to reach the net-zero CO2 emissions (NZE) within 2050 [1].
Decarbonization of transport sector is crucial for achieving Net Zero 2050, as this sector is responsible for around 21 % of global CO2 emissions (7670 Mt vs 36639 Mt in 2021) [2]. The transport sector is particularly challenging to decarbonize due to its fundamental reliance on the inputs of fossil feedstock (i.e. crude oil and natural gas), used both as energy source and raw materials to produce transport fuel.
To deeply decarbonize the transport sector, few action areas beside energy efficiency, have been considered [1]:

- Deployment of electricity to become the dominant fuel;
- Deployment of hydrogen-based fuels;
- Transformation of refineries in biorefineries by substituting oil and gas for biomass;
- Substitution of fossil fuels for biofuels.

The deployment of biofuel must be based on a circular economy policy, mainly utilizing as raw material biomass waste generated by agriculture and forestry, food industries and domestic waste. As a matter of fact the amount of energy potentially recoverable form waste biomass is huge (130-240 EJ/y) [3] , but only few is today utilized, in particular for biofuel production. The biofuels currently commercialized, i.e. bioethanol, biodiesel (FAME) and Hydrogenated Vegetable Oil (HVO), are mainly produced from raw materials competing with the food sector [4]. For this reason, critical issues from an ethical point of view have raised. Accordingly new legislation has evolved by promoting the introduction of renewable fuels produced from waste biomass (i.e. advanced biofuels, from agricultural waste such as wheat straw or corn stalks, agroforestry residues, biomass cultivated for energy use on marginal land such as miscanthus, aquatic biomass, the organic fraction of domestic waste, sludge from water purification plants, and livestock sewage) or from other waste not of biogenic origin like plastic waste. Despite the obvious advantages in terms of sustainability, renewable fuels have not yet reached large-scale commercialization, due to the high complexity of the technologies involved and the high production costs. From a technological point of view, the processes for the production of these fuels can be classified as biochemical processes (e.g. fermentation, aerobic biosynthesis, anaerobic digestion and CO2 biofixation), thermochemical processes (e.g. pyrolysis, gasification and hydrothermal liquefaction) and synthetic catalytic processes (e.g. hydrogenation, cracking, Fischer Tropsch synthesis) [5].
The presentation will illustrate the most salient technological aspects of this industrial sector, focusing on the catalysis issues.

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Catalysis for Sustainable Fuels

Pablo Beato

Topsoe, Lyngby, Denmark
pabb@topsoe.com

Keywords: Sustainable fuels, MTJet™, Hydroflex™, eREACT™, LTFT™, SAF, eFuels, eJet

Topsoe is developing and licensing process technologies and catalysts that can convert feedstocks such as renewable electricity, biomass & waste, or fossil energy into chemicals and fuels such as hydrogen, ammonia, methanol, fuels and solutions that remove sulfur. Today, Topsoe is among the top 3 in each of these market segments and no 1. in segments such as renewable fuels, hydrogen and ammonia.
The first part of this lecture will provide an overview on the status of currently available technological solutions for sustainable fuels, including an outlook into the most exciting trends and developments. In the second part the lecture will dive deeper into the actual catalytic processes behind the technologies and discuss the scientific challenges that the catalysis industry needs to master to succeed in the clean energy transition.

Biomass as feedstock for non-food applications

C. Pinel*, V. Meille, N. Perret,

IRCELYON, UMR 5256, CNRS, Université Claude Bernard Lyon1, Villeurbanne, France
**Catherine.pinel@ircelyon.univ-lyon1.fr*

Keywords: oxygenated substrates, aqueous-phase catalytic transformation**,** fine chemicals, hydrogen.

The significant climatic upheavals and the general deterioration of the environment must lead us to step back to evaluate the impact of our anthropogenic footprint and to find quickly alternatives to the productions of essential chemical compounds. In order to reduce greenhouse gas emissions, the conversion of biomass and the derived-platform molecules into synthons for fine chemistry or specialty chemical sectors is an alternative to fossil resource use.

The development of efficient catalysts within this area of research has evolved spectacularly since the beginning of the XXIst century. Significant progresses have been achieved leading to the development of highly active and selective heterogeneous catalysts. While in some applications, catalysts developed for transformation of petrochemicals may be used, in many cases, considering the chemical diversity of biomass derivatives, specific catalysts have to be developed. Indeed, aqueous-phase processing is a key issue since highly oxygenated compounds are concerned in the lignocellulosic biomass. To address this issue, the design of ideal catalysts as well as appropriate processes are world-wide studied.

We have developed a range of catalytic systems active in hydrogenation, hydrogenolysis, aerobic oxidation or dehydrogenation of oxygenated substrates issued from biomass. The nature of the support (mainly oxides), of the metal (rhodium, ruthenium, copper, molybdenum…) affected the performances of the catalysts but also the stability [1]. In addition, the influence of potential residues or impurities present in the raw feed has rarely been studied while there is a need to better understand their effect [2]. Applications covered fine chemicals (solvent, monomer or chemical intermediates) as well as hydrogen production [3].

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Materials and Mechanisms to Promote CO_2 Hydrogenation to Methanol

Malte Behrens[1*]

[1]*Institut of Inorganic Chemsitry, Kiel Nano Surface and Interface Science (KiNSIS), Kiel University, Max-Eyth-Str. 2, 24118 Kiel, Germany*

[*]*mbehrens@ac.uni-kiel.de*

Keywords: Methanol synthesis, Cu/ZnO catalyst, strong metal support interaction, catalyst promotion

Introduction. Co-precipitated Cu-based catalysts are among the most active and most widely studied catalytic materials in methanol synthesis with an increasing knowledge on the active site and the role of the Zn promoter. The precursor chemistry of the catalyst preparation has been studied in detail in our group[1] and found to be the basis for the synthesis of model materials that allow insight into the role of copper promotion by strong metal support interaction. For example, a series of Cu/MgO catalysts can be promoted by varying low amounts of Zn oxide enabling element-specific characterization of the dynamic state of Zn in the activated catalyst. Based on this insight, we derive a model for the active site, which was further investigated by selective poisoning with ammonia. Furthermore, the principles of the Cu-Mg-Zn system can be transferred to other metal/promoter combinations M-(Mg)-E, e.g. M = Cu, Ni and E = Zn, Ga.

Experimental/methodology. Catalysts were synthesized by co-precipitation from precursors such as $(Cu,Mg)CO_3(OH)_2$ with a Cu:Mg ratio of 70:30.[2,3] The promoter was added by impregnation in amounts between 0 and 20 wt%, which is low compared to the zinc content of industrial-type Cu/ZnO catalysts with a Cu:Zn ratio of ca. 70:30, which was used as a benchmark catalyst (including Al as secondary promoter).

Results and discussion. The Cu/MgO catalyst's activity in methanol synthesis from CO/H_2 was >2 times higher than that of the $Cu/ZnO/Al_2O_3$ benchmark,[2] but it was almost inactive in CO_2/H_2. The addition of Zn successfully promoted the CO_2 hydrogenation with a maximum at 10% ZnO. *In-situ* XAS at the Zn K-edge revealed the state of the promoter in the activated catalyst.[4] Together with DFT calculations, the results suggest the co-existence of reduced alloy species $Zn^{(red)}$ with partially oxidized $Zn^{(ox)}$ at the Cu surface supporting the presence of such sites also on industrial benchmark.[5] NH_3 is a probe molecule to affect the such promoted Cu sites by dosing pulses on the working industrial-type catalyst at high pressure.[6] NH_3 was found to inhibit methanol synthesis in CO_2-containing synthesis gas. During steady-state, isobaric trimethylamine (TMA) and NH_3 injections poisoned methanol formation reversibly, with the NH_3 poisoning being significantly stronger than TMA. Based on DFT calculations, NH_3 activation takes place on O* or OH* followed by the reaction with CO_2 forming a stable carbamate on the active site.[7] Further hydrogenation of the carbamate to methylamine exhibits high barriers, thus being rather slow, explaining stronger NH_3 poisoning, as TMA cannot form such carbamate species and acts only as weakly bound site-blocking species. Our contribution aims at a more detailed picture of the active site in methanol synthesis and highlights the role of the Zn promoter, which co-exists as reduced surface alloy and an oxidized form on the activated Cu catalyst. The poisoning effect of NH_3 on these active sites is explained by the presence of O*, likely on the $Zn^{(ox)}$ species, giving rise to NH_3 activation and formation of strongly bound carbamate.

Acknowledgments

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Translational Molecular Catalysis: From Challenging Catalytic Hydrogenations to Open-Loop Recycling

Jürgen Klankermayer[1*]

[1]*Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Worringerweg 2, 52074 Aachen, Germany*

[*]*jklankermayer@itmc.rwth-aachen.de*

Keywords: molecular catalysis, catalytic hydrogenation, carbon dioxide utilization, circular economy

Molecular catalysis has made tremendous advancements in the last few decades, and the implementation of modern computational methods has paved the way for the directed design of effective catalyst systems. This enabled, for example, the selective reduction of demanding functional groups in the field of catalytic hydrogenation and also the use of carbon dioxide as a renewable C1 building block in complex syntheses.[1,2,3] Recent developments pose a new challenge at the chemical–energy interface, which no longer requires the development of selective catalytic systems for bond formation, but rather for bond cleavage. Recently, various catalytic approaches for hydrogenolysis and selective bond cleavage have been established in a variety of polymers and biobased macromolecules, and in selected examples processes using waste materials from consumer products have already been implemented.[4,5] While current approaches largely focus on the combined use of carbon dioxide and molecular hydrogen to form C1 synthons, a novel methodology enables the synthesis of complex molecular structures with the combined direct integration of bio-based platform molecules or plastic waste, eventually leading to the concepts of bio-hybrid synthesis and open-loop recycling.[6,7]

Here, the challenges and opportunities of these new approaches to sustainable catalytic transformations and recycling approaches are presented. The general aspects are illustrated with current research results from our laboratories on the development, application and mechanistic understanding of molecular catalysts and catalytic systems.

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Science and Art of Successful Catalysts Promotion by Alkali

Andrzej Kotarba*

[1]*Jagiellonian University, Faculty of Chemistry, Krakow, Poland*
**E-mail address: kotarba@chemia.uj.edu.pl*

Keywords: electronic promotion, work function, surface chemistry, nanostructuration

Introduction.
Alkali metal compounds are widely used as promoters in many catalytic processes. The addition of alkali affects the catalysts' efficiency in many ways by increasing the activity, selectivity or prolonging the lifetime. Although the beneficial role of alkali additives is experimentally well established in catalysis, a more in-depth understanding of their action is still lacking. This is mainly due to their high reactivity, surface and bulk mobility, and difficulties in the characterization of their real surface states. Several aspects of alkali doping will be addressed such as surface states, electronic and structural effects, surface spreading, bulk and surface diffusion, and promoter loss via thermal desorption. Each of these issues will be illustrated with results referring to well-defined surfaces of active phases, as well as the model and industrial catalysts.

Experimental/methodology.
The investigated active phases model and real catalysts were thoroughly characterized by several traditional methods including XRD, SEM-EDX, HR-TEM/FIB, STEM/HAADF/EELS, XPS, RS, BET. The catalyst activities were measured in the laboratory (steady-state, temperature-programmed modes) and industrial conditions. In an attempt to elucidate the promotional effects of alkali and identify the decisive parameters responsible for their performance, a Species Resolved Thermal Alkali Desorption method has been developed. In tandem with work function measurements, it provides a powerful tool for the static and dynamic description of the alkali promoters in catalytic systems. The measurements were conducted in both vacuum and in near-catalytic conditions to bridge the material and pressure gap. In several cases, molecular interpretation of the results was gained by DFT modeling of the related systems.

Results and discussion.
The specific issues mentioned in the introduction are illustrated with the results referring to well-defined surfaces of active phases (e.g. Fe, Co, Ni, Co_3O_4, Fe_3O_4, $KFeO_2$, $K_2Fe_{22}O_{34}$, KMn_4O_8 KMn_8O_{16}), as well as the model and industrial catalysts (e.g. for ammonia synthesis, EBDH, ESR, DeN_2O, DeSoot). The results are discussed in terms of alkali surface state and localization (surface vs. bulk, active phase vs. support) [1, 2], electronic promotion (work function lowering) [2], structural functionalization (nanostructuration) [3], alkali dynamics (bulk diffusion, surface segregation, desorption) [4]. The effects of alkali promotion are explained at the molecular level for several investigated catalytic systems. Finally, an overview of reactivity descriptors and rational guidelines for designing, optimizing, and testing alkali-promoted catalysts are outlined.

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Sustainable Homogeneous Catalysis Using Sustainable Safer Solvents

David E. Bergbreiter

Chemistry Department, Texas A&M University, College Station, TX 77843 USA
E-mail: bergbreiter@tamu.edu

Introduction. Greener and/or more sustainable chemistry can involve many factors. However, a paramount issue is sustainability. That involves catalyst and solvent sustainability. Catalyst sustainability can be an issue because of the use of precious metals or complex ligands. Solvent sustainability is an issue because solvents are the major component of most reactions.

Experimental/methodology. In a typical experimental procedure, a PAO-soluble polyisobutylene hydrocarbon oligomer is modified by known chemistry to attach a catalyst or a ligand and a catalyst.[1] This catalyst is then dissolved in a PAO solvent, typically a C_{20}, C_{24}, or C_{30} PAO.[2] A substrate is then added with a functionalized PIB or an added low molecular solvent to enhance substrate solubility. Then the catalytic reaction is carried out using the same procedure that would be used for a low molecular weight catalyst. After the reaction, the product is removed either by distillation, a solid/liquid separation (if the product precipitates), or by a liquid/liquid separation using a PAO immiscible solvent like CH_3CN. Subsequent cycles involve addition of fresh substrate.

Results and discussion. Our work has approached the problem of making homogeneous catalysis more sustainable by focusing on making recycling catalysts, ligands, and solvents as simple and as quantitative as possible. Our thesis is that a properly designed fully recyclable system of catalysts and solvents can simultaneously address issues of both catalyst and solvent sustainability. In the case of catalysts, we have focused on using polyolefins like polyisobutylene as phase anchors to recycle catalysts and ligands. For solvents, we have been exploring inexpensive safer, separable, and recyclable solvent systems that use polyolefins. Our work has shown that low viscosity commercially available the poly(alpha-olefin)s (PAOs) - fractionated hydrocarbon mixtures with 20-48 carbons - have considerable potential as solvents in synthesis and separation chemistry.[2] Such PAO solvent systems with polyolefin-bound catalysts fulfill several criteria for green and sustainable chemistry. The PAO solvent serves as a recyclable, regenerable sequestering phase. PAO phases with PAO-soluble catalysts, reagents, and sequestrants can be quantitatively recycled multiple times in catalysis, synthesis, and separation chemistry without significant contamination of the isolated organic products or of a separable polar solvent phase. Separations can most often be accomplished by liquid/liquid or liquid/solid separations. PAOs safer solvents too because of their high flash point and low volatility.[3] In moist examples, catalysts using this process can be recycled at least 5-10 times with no loss of the PAO solvent. Catalyst leaching in the separations is typically minimal. This talk will highlight these themes with examples of various transition metal and organocatalysts, pointing out both advantages and this advantages of this approach to sustainable homogeneous catalysis.

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Magnetic Catalysts and Catalytic Magnets: Never the twain?

Evgeny Rebrov[1,2*]

[1]*Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, the Netherlands*
[2]*School of Engineering, the University of Warwick, Coventry, UK*
[*]*e.rebrov@tue.nl, e.rebrov@warwick.ac.uk*

Keywords: magnetic superstructure; inductive heating; hydrogen evolution reaction (HER); magnetic catalysts, forced periodic modulation.

Introduction. The inductive heating of catalysts impregnated with magnetic susceptors or magnetic susceptors functionalized with catalytic active centers have been exploited for a wide range of applications, spanning from fine chemicals synthesis to electrochemistry. Whatever the application, induction heating provides unique features in comparison to conventional heating systems based on heat convection or conduction. With inductive heating, high temperatures can be reached more quickly on the active centers while the surface coverages need more time to adjust to the new conditions. This creates a possibility to run the reaction under forced periodic modulation of temperature and other parameters (flow rate, concentrations) such that the time averaged reaction rate or/and selectivity could considerably exceed those obtained at steady-state conditions [1].

Results and discussion. There exists two fundamentally different approaches for preparing supported catalysts operated under inductive heating. In the first approach, magnetic susceptors with excellent heating power (such as $Fe_{2.2}C$, $Co_{60}Ni_{40}$ etc.) are functionalized with a support layer (SiO_2, TiO_2) and then with catalytic nanoparticles [2]. In this approach, controlled surface engineering is vital for the design of stable catalysts. Usually, macroscopic ferromagnetic alloys are used as susceptors of magnetic field in highly endothermic transformations. In the second approach, conventional catalysts are in-situ grown around the magnetic nanoparticles [3] or magnetic nanoparticles are embedded in the catalyst support in a post-synthesis step [4]. Ferromagnetic materials (like iron oxide, nickel and cobalt ferrites) are usually employed. The control of magnetic material structure at the nanoscale is the key to increase performances and improve the energy efficiency under induction heating. Sometimes a combination of these two approaches is used when a support is coated with magnetic and catalytic materials [5]. In this respect, the development of functionalization treatments of high quality to yield magnetic catalysts with superior properties still remains a largely unexplored field, even when significant progress has been reported in the use of different organic and inorganic passivation or functionalization agents.

In this presentation, we will discuss main synthetic methods for preparation of composite magnetic catalysts, followed by their characterizations and applications in fine chemical synthesis, hydrogenation of bio-oil and electrochemistry (hydrogen evolution reaction) [6], where the reaction rate and/or selectivity was considerably increased as compared to conventional operation.

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Ceria Nanoparticles Shape Effects in Catalysis

Michalis Konsolakis*

School of Production Engineering and Management, Technical University of Crete, GR-73100, Chania, Greece
**E-mail : mkonsolakis@tuc.gr*

Catalysis is an indispensable part of our society, being massively involved in numerous energy and environmental processes of paramount importance. In fact, catalysis constitutes a field of diverse applications, including, among others, the production of high-commodity chemicals and fuels, refining and petrochemistry and abatement of hazardous substances, all playing a key role towards sustainability. In view of this fact, the rational design and development of cost-efficient catalyst formulations with tailored reactivity constitutes the main research pillar in the field of catalysis. Towards this direction, the fine-tuning of local surface chemistry by means of advanced synthetic and promotional routes has recently gained particular attention. In specific, the adjustment of size, shape and electronic state of multi-component metal oxide systems at the nanoscale though appropriate synthesis methods and nano-engineering strategies can exert a profound influence not only to the reactivity of metal sites, but to the interfacial activity as well, resulting in the development of highly active and stable materials for real-life energy and environmental applications [1-3].

In the present talk, the pivotal role of shape engineering in catalysis is exemplified on the basis of transition metal catalysts based on CeO_2. Initially, the underlying mechanism of the facet-dependent reactivity of ceria nanoparticles is discussed. A thorough characterization study of ceria-based composites of distinct nano-morphology (rods, cubes, polyhedra) is presented next, so as to gain insight into the impact of different exposed facets into key physico-chemical properties. It is clearly disclosed that shape functionalization can notably affect several key activity descriptors with direct catalytic implications. Most importantly, the combination of ceria particles with specific nano-arcitecture with late 3-d transition metals may very well induce synergistic metal-ceria interactions, thus offering extremely active and stable catalytic composites for various heterogeneous processes. Besides, from a practical standpoint, novel catalyst formulations with similar or even superior reactivity to that of noble metal-based catalyst may be obtained, such as Cu/CeO_2-nanorods for oxidation reactions and Ni/CeO_2-nanorods for CO_2 hydrogenation processes [4-8]. Last but not least, an overall rationale and design guidelines towards the fabrication of earth-abundant metal oxide catalysts for application in various chemical reactions of energy and environmental significance are provided.

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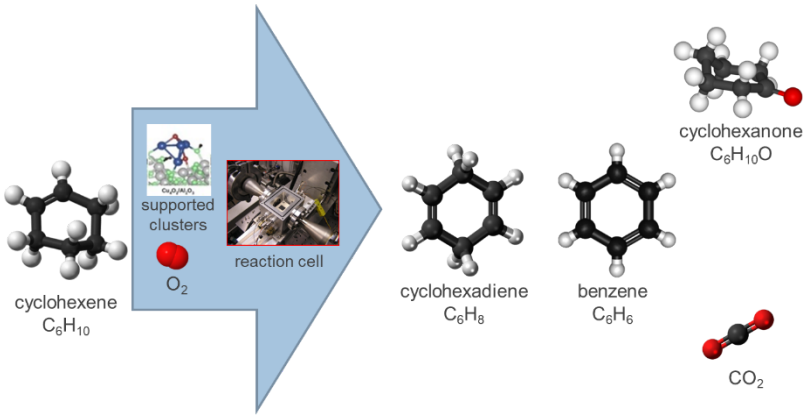
Size- and Composition--Selected Subnanometer Cluster Catalysts in Oxidative Dehydrogenation and Hydrogenation Reactions

Štefan Vajda

Department of Nanocatalysis
J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences
Dolejškova 2155/3, 182 23 Prague 8, Czech Republic
stefan.vajda@jh-inst.cas.cz

The focus of the presentation will be on catalysts by supported monodisperse subnanometer clusters made of a handful of atoms, supported on technologically relevant oxide- and model carbon-based supports.



The performance of Co, Cu, Pd and CuPd clusters in the oxidative dehydrogenation of cyclohexene and cyclohexane will be discussed [1-4], where the atomic precision design of mono- and bimetallic clusters allows for the fine-tuning of their activity and selectivity by varying the composition of the clusters in an atom-by-atom fashion and by support effects.

In the second part of the presentation, the conversion of CO_2 on copper cluster-based catalysts to methane vs methanol or longer chain hydrocarbons will be discussed in the dependency of cluster size and support used.[5-7]

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Catalysis at the metal-support interface: about nanoparticles, clusters and single metal atoms

Emiel J.M. Hensen*

Laboratory of Inorganic Chemistry and Catalysis, Department of Chemical Enigneering and Chemistry, Eindhoven University of Technology, The Netherlands

Heterogeneous catalysis significantly shapes society, as it plays a crucial role in the production of fuels for mobility and base and specialty chemicals. C1 chemistry is expected to be pivotal in the transition to a sustainable reality in which renewable feedstocks and energy replace fossil resources. Typical heterogeneous catalysts for the activation of small molecules like CO, CO_2 and CH_4 consist of "metal on a support". Structure sensitivity refers to the dependence of chemical reactivity of metal nanoparticles on size and often implies low catalytic efficiency. Overcoming such limitations of structure sensitivity can be achieved by systems in which metal – metal-oxide interfaces form the active sites. These include metal oxides dispersed on metal nanoparticles as well as ultra-dispersed metal phases on redox-active support materials for the activation of reactants. Experiment and theory will be combined in this lecture with CO_2 hydrogenation as a model reaction relevant to renewable energy storage.

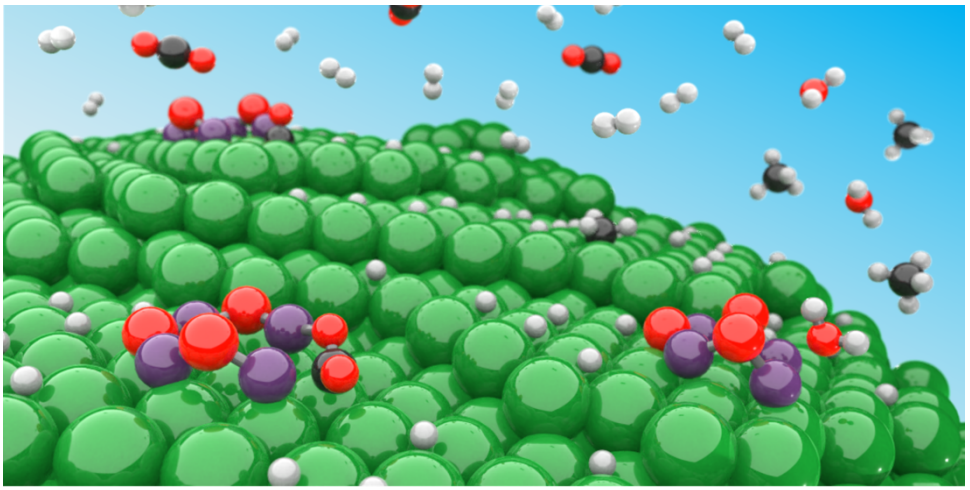

Figure 1: Structure sensiitivity guides the design of metal nanopartticle catalysts for sustainable catalysis.

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Engineering of Catalytic Cycles in Redox Reactions

De Chen

[1] Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, 7491, Norway. *de.chen@ntnu.no*

Keywords: redox cycley, operando kinetic study, rational design of catalysts

Introduction. Redox reactions play a critical role in the chemical industry and are used in numerous industrial processes, including the production of chemicals, fuels, and metals, as well as environmental applications. Understanding the mechanisms of these reactions and developing efficient and sustainable catalysts is essential for the continued growth and advancement of the chemical industry. The oxidation state of metal plays a crucial role in determining the activity, selectivity, and stability of catalytic redox reactions, which are essential in many industrial processes. The engineering of the catalytic cycle of redox reactions requires a deep understanding of the redox mechanisms involved and the ability to control the oxidation state of the metal. In this context, the Mars and van Krevelen mechanism provides a simplified approach to understanding redox cycles in selective oxidation reactions. Many redox reactions involving C, Cl, N, and S follow similar simplified mechanisms on metal carbide, chlorides, nitrides and sulfides.

Experimental/methodology. A new approach for kinetic analysis and rational design of the redox reaction cycle, as well as a new tool for predicting the catalyst's oxidation state, were developed. The approach involves the oprando transient kinetic study and modeling of individual reduction and oxidation steps following a kinetic synthesis of the redox cycle at the steady state . The operando kinetic study was carried out in a fixed bed reactor coupling with in-situ UV-Vis-Near IR and mass spectroscopies

Results and discussion. The approach can help in optimizing catalyst performance and predicting catalyst behavior in industrial reactors. The control of the oxidation state of the metal can be achieved through the selection of appropriate catalysts, the use of promoters or inhibitors, and the manipulation of reaction conditions. The engineering of the catalytic cycle of redox reactions provides a new tool for the rational design and fine-tuning of the metal oxidation state for the development of efficient and sustainable chemical processes. Applications of the approach in cases of ethylene oxychlorination and methane selective or total oxidation will be discussed.

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(Photo)electrocatalysis: facing the challenge of extending its use to go beyond fossil fuels

C. Genovese, C. Ampelli, G. Centi and S. Perathoner*

The University of Messina and the European Research Institute of Catalysis aisbl, Messina/Italy and Brussels/Belgium
** E-mail: siglinda.perathon@unime.it*

Keywords: electrocatalysis, photoelectrocatalysis, renewable energy, artificial leaf, electrocatalytic cells

Introduction. Defossilization of chemical production to meet targets such as net-zero emissions by the year 2050 is a challenge influencing research directions [1]. Electrochemistry has been known for over a century. Still, the interest in electrocatalysis raised recently, with exponential growth over the last two decades reaching over 600 publications and 25000 citations per year. Notwithstanding this impressive number of publications and reviews, the reactions investigated are mostly restricted to the conversion of small molecules (CO2, N2, H2O) and a few biomass intermediates. Regarding reactors and experimental conditions, literature studies are often quite far from those necessary for possible industrial exploitation [2,3]. Addressing the challenge of creating new fossil-free chemistry requires exploring novel solutions and approaches by identifying the limiting factors for exploitability and studying how to overcome them [4].

Discussion. This study highlights the contribution and discusses recent research projects in this area of (photo)electrocatalysis, which are relevant case examples to explore new directions but are characterised by a little background research effort. It is organized into two main sections, where selected examples of innovative directions for electrocatalysis and photoelectrocatalysis are presented.
The areas discussed include (i) new approaches to green energy or H_2 vectors, (ii) the production of fertilisers directly from the air, (iii) the decoupling of the anodic and cathodic reactions in electrocatalytic or photoelectrocatalytic devices, (iv) the possibilities given by tandem/paired reactions in electrocatalytic devices, including the possibility to form the same product on both cathodic and anodic sides to "double" the efficiency, and (v) exploiting electrocatalytic cells to produce green H_2 from biomass. The examples offer hits to expand current areas in electrocatalysis to accelerate the transformation to fossil-free chemical production. The role of the design of the cell and electrodes, and critical factors determining the behavior are also discussed.
The final part of the lecture will discuss the recent results as part of the EU project A-LEAF of the development of an artificial leaf device built with earth-abundant materials for combined H_2 production and storage as formate with efficiency >10% [5].

Acknowledgements
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Metal-organic Frameworks as versatile solar photocatalysts for overall water splitting

Hermenegildo García

Instituto Universitario de Tecnología Química, Consejo Superior de Investigaciones Científicas-Universitat Politecnica de Valencia, Universitat Politecnica de Valencia, Av. de los Narnajos s/n, 46022 Valencia, Spain
**E-mail: hgarcia@qim.upv.es*

Keywords: Photocalysis, Solar Energy Conversion, Overall Water Splitting, Hydrogen Generation, Metal-Organic Frameworks.

Introduction. Sunlight can provide enough energy to power the planet. However, several issues including intermittency and low power density have to be overcome. One possibilities is the storage and concentration of solar energy into chemical compounds that can be used as fuels (*solar fuels*).

Results and discussion. The fundamentals of the mechanism of the photocatalytic overall water splitting will be presented together with a short introduction on the properties of metal-organic frameworks (MOFs) that make these porous crystalline inorganic-organic materials suited for their use as photocatalysts. The main emphasis of the presentation will be on the recent contribution of the Valencia group to the field of hydrogen generation from water that has been recently summarized in Chem. Rev.[1] It will be shown how the structure of the MOF can be optimized by selection of appropriate linkers,[2, 3] metal nodes,[4] presence of co-catalysts,[5] and on-purpose generation of defects,[6] resulting in enhancements of the photocatalytic efficiency. Fig. 1 shows the structure of one of the most active materials reported so far, denoted as IEF-11.[7] IEF-11 is constituted by 2D layers of three different types of TiO_6 octahedra that are coordinated with squarate ligands in the perpendicular direction. Due to its color, squarate introduces visible light photoresponse and upon light absorption, this aromatic cycle injects electrons onto the TiO_2 layer, leading to charge separation. As result, IEF-11 exhibits a productivity in overall water splitting of 550 micromoles of $H_2/g_{catalyst}$ with the corresponding half the amount of O_2. The solid was reused ten times reproducing the same temporal profile for H_2 and O_2 evolution. Furthermore, no changes in the XRD of the solid after extensive use was observed, implying that the MOF structure remains unaltered during the photocatalytic reaction. Further improvements on the efficiency are expected upon modulation of the MOF structure. Current target is to produce over 1 mmol H_2/g_{IEF-11} under natural light irradiation, bringing photocatalytic hydrogen generation closer to TRL 5.

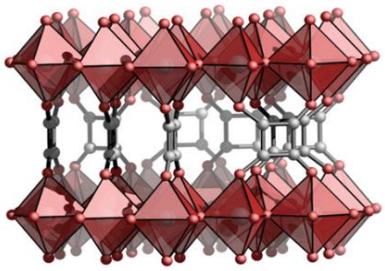

Fig. 1. Cross sectional view of IEF-11 showing the 2D TiOx layers connected by perpendicular squarate linkers (taken from ref. 7)

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Cleaning emissions from vehicles using catalysis

L. Olsson*

Chemical Engineering, Competence Centre for Catalysis, Chalmers University of Technology Gothenburg, Sweden

*louise.olsson@chalmers.se

Keywords: NOx removal, ammonia selective catalytic reduction, passive NOx adsorbers, catalyst aging

Introduction.

Exhaust from gasoline engines can be treated using a three-way catalyst, that operates in stoichiometric conditions and effectively can remove CO, hydrocarbons, and NOx. However, the exhaust aftertreatment system (EATS) for diesel and lean burn engines are much more complicated due to the difficulty in removing NOx in oxygen excess [1]. Ammonia selective catalytic reduction (SCR) is a key technology in this respect, where ammonia selectively reacts with NOx. However, there are challenges with this technique such as sulfur poisoning for example [2]. In addition, the ammonia is produced from urea decomposition and urea cannot be dosed at low temperature due to issues with deposits. An interesting technique is therefore passive NOx adsorbers, where NOx is adsorbed at low temperature and released at higher temperatures where the urea can be dosed. However, also this technique has challenges such as deactivation in the presence of high CO concentrations.

Experimental/methodology.

Different copper and palladium based zeolites were prepared. The activity, selectivity and deactivation were measured using flow reactors equipped FTIR. The catalysts were characterized in detail before and after poisoning using for example BET, XRD, XPS, TEM, TPR, TPD, DRIFTS and NMR.

Results and discussion.

An overview will be given regarding cleaning emissions from vehicles. A special focus will be given to the removal of NOx during oxygen excess. Sulfur poisoning is a large issue for Cu/zeolites that are used for ammonia SCR. In Cu/zeolites there are different types of copper species, where $[Cu(OH)]^+$ and Cu^{2+} are very important. We have found that $[Cu(OH)]^+$ is more sensitive to SO_2 poisoning than Cu^{2+}. Moreover, Cu/LTA can store larger amount of SO_2 compared to Cu/SSZ-13, which could be due to that the interaction of $[Cu(OH)]^+$ with the framework in Cu/LTA is much weaker as suggested by H_2-TPR. This results in a slower deactivation during SCR conditions [2]. Another degradation mode is phosphorus poisoning, where $[Cu(OH)]^+$ in Cu/SSZ-13 were poisoned significantly, resulting in low temperature deactivation. Moreover, the extent of phosphorus deactivation was influenced by the choice of zeolite, where Cu/BEA even exhibited increased activity due to phosphorus. XPS characterization revealed that most of the phosphorus on Cu/BEA was in the form of P_2O_5, and we suggest that P_2O_5 enhanced the redox ability [3]. Another issue with ammonia SCR is that the urea cannot be dosed at low temperatures due to deposits. Passive NOx adsorption is an interesting concept where NOx is stored at low temperature and released thermally at higher temperature when the SCR system is operating. However, there are challenges with this system, especially deactivation induced by high CO concentration. We have developed a kinetic model that can describe this CO-inducted degradation [4]. Moreover, we have developed an improved Pd/SSZ-13 catalyst, by changing the synthesis procedure which resulted in a catalyst more resistant to CO deactivation [5].

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Green asymmetric organocatalysis

Radovan Šebesta

Comenius University Bratislava, Faculty of Natural Sciences, Mlynska dolina, Ilkovičova 6, 842 15 Bratislava, Slovakia, e-mail: radovan.sebesta@uniba.sk

Climate change and enduring need for the synthesis of chiral compounds present new challenges to organic chemistry and catalysis. Efficient synthesis of chiral compounds necessary for medicines, materials, or crop protection need not only be highly stereoselective but must comply with stringent environmental criteria. The ideal synthesis should abide by principles of green chemistry such as the elimination of dangerous compounds, decrease waste production but also time and financial effectivity. Asymmetric organocatalysis, that is the use of small chiral organic molecules as catalysts, offers excellent opportunities in the synthesis of critical chiral compounds and, at the same time, enables the implementation of green chemistry principles [1].

Enantioselective organocatalytic reactions, such as Michael additions of aldehydes to nitroalkenes, aminoxylation, and hydrazination of aldehydes can be performed in aqueous media or under solventless conditions using a ball mill [2]. We have found out that these reactions proceed with high yields and highly enantioselective. The solventless methodology also allows for more effective catalysis using organocatalysts, which employ non-covalent interactions for activation [3]. Chiral thioureas and squaramides, in some cases, proved to be more enantioselective catalysts for Michael additions under solventless conditions than in solvents [3]. Ball-milling was highly effective in promoting diastereodivergent oxa-Diels-Alder reaction of unsaturated ketones with enoates [4]. Chiral squaramides were very effective for enantioselective domino Mannich reaction with fluorination [5]. We have used acidic ionic liquids and microwave irradiation to release unstable alkyloxyacetaldehydes from the corresponding acetals in situ. This idea improved the organocatalytic synthesis of antiviral drug oseltamivir [6]. Greener solvent alternatives, such as 2-methyltetrahydrofurane allow highly enantioselective warfarin synthesis [7].

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Intensification of Catalytic Processes for the Synthesis of Hydrocarbons from Renewable Feedstocks

S. Escolástico[1], M. Balaguer[1], L. Almar[1], J.M. Serra[1], A. Martínez[1*]

[1]*Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas (UPV-CSIC), Valencia, Spain*
[*]*amart@itq.upv.es*

Keywords: Renewable fuels and chemicals, intensification, membrane reactor, tandem catalysts.

Summary. The European Commission has recently adopted new net emission targets for 2030 and 2050 as part of the European Green Deal plan towards climate neutrality. Two key strategies for reaching the ambitious goal of net-zero carbon emissions include the use of renewable energy to displace fossil energy and the implementation of *Carbon Capture and Utilization* (CCU) technologies. CCU brings potential to mitigate carbon emissions by using CO_2 captured from fossil- and bio-based industries or directly from the air as a carbon feedstock for the production of value-added products. Among the available CCU options, the thermocatalytic conversion of CO_2 via hydrogenation to fuels and chemicals using green H_2 and renewable electricity is especially appealing as it provides an effective means to store and transport surplus renewable electricity in the form of chemical energy. However, most current CO_2-to-hydrocarbons conversion technologies rely on multi-step approaches involving several separation and catalytic processes (e.g., water electrolysis, conversion of CO_2 to intermediate products, transformation of the intermediates to final products) that result in low overall energy efficiency and high cost. In this respect, process intensification can provide an effective solution to these drawbacks and could thereby help to lay the ground towards their industrial implementation.

In this Keynote, the application of the process intensification concept for the synthesis of valuable hydrocarbons (e.g., fuels, chemicals) from CO_2 will be discussed from two perspectives: 1) the use of advanced multifunctional catalysts enabling the one-step hydrogenation of CO_2 to specific hydrocarbons via tandem catalysis (Figure 1), and 2) the use of electrochemical catalytic membrane reactors (e-CMRs) combining chemical reaction and separation (Figure 2). The benefits of both intensification approaches will be illustrated for the synthesis of different renewable hydrocarbons as proposed, for instance, in the two ongoing EU-funded eCOCO2 and CO2SMOS projects.

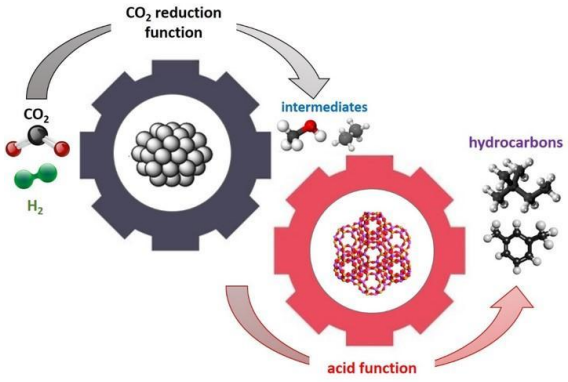

Figure 1. One-step hydrogenation of CO_2 to valuable hydrocarbons via tandem catalysis.

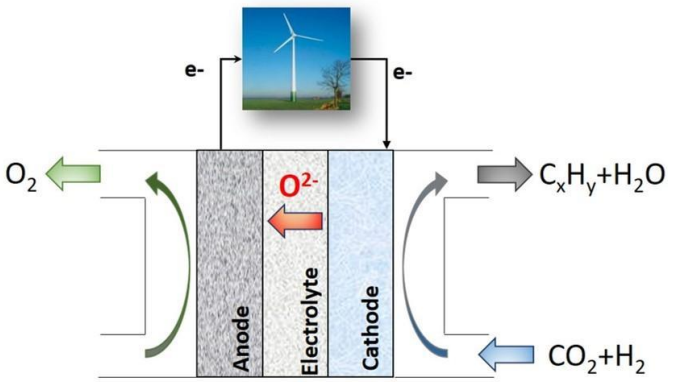

Figure 2. CO_2 hydrogenation to hydrocarbons on e-CMR with *in situ* extraction of water co-product.

Acknowledgments

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Nano-imaging chemical properties of zeolite catalysts

M.B.J. Roeffaers[1*]

[1]*cMACS, KU Leuven, Leuven, Belgium*

Keywords: fluorescence microscopy, correlative microscopy, Raman microscopy, nanoscale structure-function-activity relation

Introduction.

Fluorescence microscopy is a recent addition to the toolbox for in situ study of solid catalytic materials. It combines ease of use with non-invasiveness, high sensitivity, and temporal resolution.[1,2] In this presentation, I will explain how fluorescence-based assays can be used to map catalytic reactions inside individual zeolite particles down to the single turnover level. Such measurements, in combination with structural and functional information from correlative Raman and electron microscopy, enable to generate nanoscale activity images of working zeolite catalysts.[3,4] Next to significant intraparticle heterogeneities, the data also reveal important interparticle heterogeneities, which have often been overlooked so far, and this both for lab-scale and industrially produced catalyst batches.

Results and discussion.

Fluorescence microscopy is widely used in biomedical research, however, its use in materials research is much less explored. In contrast to biological (single molecule) fluorescence studies, that rely on large polycyclic substrates, the widespread application in catalysis research critically depends on identifying relevant reagent molecules that are converted into strongly fluorescent reaction products that are detectable with single-molecule sensitivity.[1,2] By recording the fluorescence signal generated by every single catalytic conversion and by accurate image reconstruction, a nanoscale activity map can be generated. Overlaying such information on the corresponding electron micrographs enables to precisely pinpoint the zones of enhanced catalytic activity.

Next to the direct observation of catalytic conversions, a detailed understanding of catalytic site distribution and accessibility is critical. Rather than looking at the inorganic compositions, as in electron and X-ray microscopy, we employed advanced Raman-based assays with organic probe molecules similar to those used in infrared spectroscopy to visualize the 3D acid site distribution in acid zeolite catalysts.[4]

In this contribution, information on single zeolite crystals obtained from different types of optical microscopy will be combined to generate a detailed picture of working zeolite catalysts (ZSM-5[5,6], MOR[4,7] and USY [8]) at the single particle level and ultimately with single-molecule sensitivity. The presented approach enables unraveling the complex interplay between diffusion, catalytic site distribution, and reactions at the single particle level. Furthermore, next to significant intraparticle heterogeneities, the data also reveal important interparticle heterogeneities which have often been overlooked so far.

Acknowledgments

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Heterogeneous catalysts under pressure

Jeroen A. van Bokhoven[1,2]

[1]*ETHzurich, Zurich, Switzerland*
[2]*Paul Scherrer Institute, Villigen, Switzerland*
[*]*j.a.vanbokhoven@chem.ethz.ch / jeroen.vanbokhoven@psi.ch*

Keywords: heterogeneous catalysis, characterization, pressure gap, materials gap

Introduction.

The continued quest for novel and better catalysts is helped by providing an understanding of the relationship between structure and properties. The obvious difficulties to obtain such relationships are, on the one hand, the complexity of the heterogeneous catalyst and, on the other, the demanding conditions under which catalytic reactions are performed. One understandable approach is to make use of model systems and to employ milder reaction conditions. Oppositely, doing so may lead to erroneous conclusions when extrapolating results to actual catalysts and conditions.
Methanol synthesis from synthesis gas is done over archetype $Cu/ZnO/Al_2O_3$ catalyst, the structure of which is debated since decades. There is renewed interest in the catalyst, given its activity in methanol synthesis from carbon dioxide and renewable hydrogen. Such green route with methanol as intermediate towards fuels and chemicals may play a future role in chemicals and fuels production. There are multiple catalytic functions that the catalyst must fulfill. Through characterization at various pressures, a very complex relationship between catalyst structure and condition is identified.

Experimental/methodology.

Through systematically varying the pressure of hydrogen on the one hand and of CO_2/H_2 mixtures on the other, the complex interplay between structure and pressure is identified. The combination of high-pressure isotope exchange experiments, joint by simultaneous infrared spectroscopy, and operando XAS at the Cu and Zn K edges, the reaction mechanism and its relation to catalyst structure emerge.

Results and discussion.

The conditions at which alloy formation occurs are identified, as well as the roles of surface adsorbates and the structures that copper and zinc adopt under various conditions. Based on these data will activity - performance relations be drawn. In addition, including simple considerations the limitations of such conclusions will be discussed, which will be positioned into a general perspective to what extend we have achieved actual understanding of functioning heterogeneous catalysts.

Catalysis for sustainable chemical production

A. Kirilin[1]

[1]*Dow Benelux B.V., Corporate R&D, Terneuzen, the Netherlands*
akirilin@dow.com

Introduction.

Climate changes, energy and feedstock cost and availability are among major global challenges that are vital to our society. The chemical industry is at the front end of innovation [1] to develop more sustainable, energy efficient and cost competitive solutions [2] with purpose to meet ambitious recycling, circularity and decarbonization goals and deliver a sustainable future for the world.

Catalysis plays a critical role in enabling chemical transformations that otherwise would not be possible. Catalytic technologies can provide energy advantaged solutions with reduced CO_2-footprint compared to non-catalytic routes.

Results/Discussion.

To illustrate the role and importance of heterogeneous catalysis and innovation in the industrial sector, two examples of catalytic chemistries will be discussed. The first example is the use of synthesis gas (mixture of CO and H_2) as versatile platform enabling use of recycled carbon for the production of feedstocks and platform chemicals (ethylene, propylene) via catalytic routes. In particular, a hybrid catalyst approach for syngas conversion will be highlighted. Hybrid catalysts comprise a mixed metal oxide (MMO) and a zeolite component that are working in tandem. The aspects of rational catalyst design with respect to catalyst selectivity and stability will be discussed [3].

Another example covers a novel route for synthesis of methyl propionate (MP), an important chemical used as solvent, additive in coatings and used in production of other industrial chemicals. One of the commercial technologies to produce MP today is liquid phase process that uses a homogeneous palladium-based catalyst. Use of expensive homogeneous catalysts, need for handling and purification of solvent as well as separation costs make the overall process energy intense.

Dow has envisioned a more sustainable and energy efficient route for methyl propionate production based on C2 feedstock platform in a gas-phase process using a heterogeneous catalysis. A single-step transformation of ethylene, CO and methanol directly to methyl propionate is enabled thru metal sulfide catalysts [4] without a need to use noble metals. A combination of catalytic approach, high selectivity to target product and ability to efficiently recycle unconverted feedstock results in reduction of energy intensity and increase in overall process efficiency compared to the traditional Pd homogeneous catalytic process.

Acknowledgments
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Electrophotocatalysis: Combining Light and Electricity to Promote Reactions

T. H. Lambert[1*]

[1]*Cornell University, Ithaca, NY, USA*
[*]*tristan.lambert@cornell.edu*

Keywords: electrophotocatalysis, photocatalysis, electrochemistry

Introduction. Visible light photocatalysis and electrocatalysis have emerged as two prominent approaches for driving chemical reactions. However, the combination of these modalities, known as electrophotocatalysis, has remained relatively unexplored until recently. In the past few years, a growing number of studies have showcased the immense potential of harnessing both light and electrical energy to enable novel catalytic transformations. Electrophotocatalysis eliminates the need for large amounts of chemical oxidants or reductants by utilizing an electrochemical potential as an electron source or sink, thereby enabling efficient photoredox reactions. In addition, electrophotocatalysis also readily enables the use of open-shell photocatalysts, which typically possess very high redox potentials, leading to powerful redox reactions under mild conditions. This lecture will describe some of our work in the area of electrophotocatalysis, especially using trisaminocyclopropenium (TAC) ions.

Experimental/methodology. We have shown that a trisaminocyclopropenium ion (TAC^+) can serve as a powerful oxidative electrophotocatalyst.[1] Mechanistically, the TAC cation (TAC^+) can be oxidized at a relatively low anodic potential (1.26 V vs. Standard Calomel Electrode, SCE) to produce the deep red TAC radical dication ($TAC^{\bullet 2+}$). When photoexcited, this species becomes a powerful oxidant ($TAC^{\bullet 2+*}$, 3.33 V vs. SCE). Thus, irradiation of an electrochemical cell containing TAC^+ can oxidize even poorly reactive substrates via single electron transfer (SET) to generate the corresponding radical cations, which are highly reactive intermediates that can lead to a number of advantageous reaction outcomes.

Results and discussion. TAC electrophotocatalysis has enabled a range of transformations, including the oxidative functionalization of unactivated arenes, the regioselective derivatization of ethers, C–H aminations, vicinal C–H diaminations and dioxygenations, olefin dioxygenations and aminooxygenations, and carbonyl olefinations. These results, along with insights into catalyst stability and operation, will be discussed.

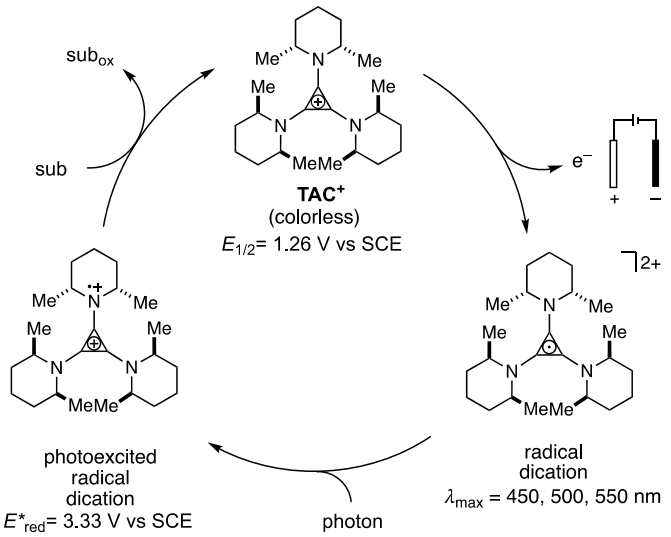

Figure 1. Trisaminocyclopropenium (TAC) electrophotocatalysis.

Acknowledgments
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Adventure in Homogeneous catalysis : from laboratory to industrial applications

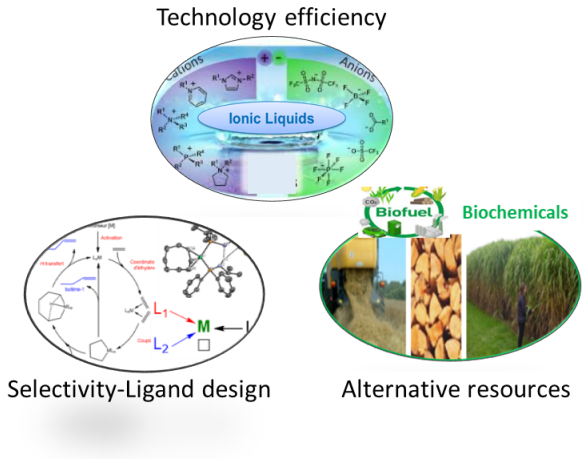
Hélène Olivier-Bourbigou

IFP Energies nouvelles, 1&4 Avenue de Bois-Préau, 92852 Rueil-Malmaison, France
helene.olivier-bourbigou@ifpen.fr

Keywords: petrochemistry, ionic liquids, biomass conversion

Petrochemistry is an essential part of the chemical industry today. The production of petrochemicals and their derivatives which are integral to modern societies and found in many parts of the modern energy system, absorbs an increasing proportion of the world's oil and gas (approximately 14%) with a global demand growth faster than oil's. What could be the research and innovation contribution to make petrochemistry more sustainable ?

In this context, the presentation will particularly focus on 3 parts. The first one will concern the technology efficiency. The development of ionic liquids will be discussed for olefin transformation (metal-catalyzed and acid-catalyzed oligomerization and hydroformylation) with new developments of catalytic systems that bridge the gap between homogeneous and heterogeneous catalysis [1]. The second part will focus on how to improve feedstock efficiency in increasing selectivity for the production of on-purpose alpha-olefins with ligand oriented catalyst design approach [2-3]. In the third part we will outline the possible alternatives to fossil resource for the production of fuels and chemicals [4]. Non-edible biomass chemistry is considered to represent a realistic option with bio-ethanol as an interesting platform molecule that can bridge the gap between biomass fuel production and traditional petrochemical engineering.



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Awards

How Artificial Intelligence and Knowledge Graphs will change Development Workflows in Catalysis

Stephan Andreas Schunk [1*, 2, 3]

[1]*hte GmbH, Heidelberg, Germany*
[2]*BASF SE, Heidelberg. Germany*
[3]*Universität Leipzig, Institute for Technical Chemistry, Leipzig, Germany*
[*]*stephan.schunk@hte-company.de*

Keywords: catalysis, high throughput experimentation, artifical intelligence, sustainability

Catalysis plays a crucial role as core technology in helping achieve the United Nations' sustainability goals, particularly in reducing greenhouse gas emissions, integration of secondary biomass and promoting recycling of various waste forms. This is because catalysts can help improve the efficiency of chemical processes, reducing energy consumption and emissions of greenhouse gases such as carbon dioxide, methane, and nitrogen oxides and therefore promote circular economy. Additionally, catalysts can be used to convert greenhouse gases into valuable chemicals, helping to remove them from the atmosphere.

A massive change is at the horizon for development workflows in catalysis, which is in at large driven by the availability of Big Data in catalysis in harmonized formats and the ability to analyze these data and to predict system behavior down to the molecular scale.

Development workflows in the field of catalysis are likely to evolve in the future in several ways:

-Increased use of artificial intelligence (AI) and machine learning in predicting behavior on molecular scale for materials and molecules: AI and machine learning algorithms will play an increasingly important role in catalyst discovery, optimization, and design, automating many tedious and time-consuming tasks. AI

-Integration of computational simulations: Computational simulations, particularly high throughput simulation augmented by AI, will therefore become increasingly integrated into development workflows, allowing for the prediction and optimization of catalytic behavior before synthesis and experimentation. Simulation results can easily be democratized and shared. A culture of sharing is also already better embedded in the community of practice in the field of theoretical chemistry.

-High-throughput experimentation plays an increasingly pivotal role in these development cycles: hte methods are becoming more widespread, enabling the rapid screening of large numbers of catalysts and reaction conditions and will be the most valuable resource of trusted experimental data – available as Big Data.

Several approaches which can lead to new materials using Big Data generation and analysis and high precision modelling and prediction will be presented and discussed in this lecture.[1]

[1] This text has been generated using AI based methods with minimal human curation exercise and editing. This exercise has been concluded within the framework on an internal project around the topic “AI in Chemistry”. The presentation of the result seeks not to offend the organizers and participants of the conference but should be seen as a general view on where AI in Chemistry stands today.

On the structural sensitivity of platinum electrocatalysts

Federico Calle-Vallejo[1,2,*]

[1] *Nano-Bio Spectroscopy Group and European Theoretical Spectroscopy Facility (ETSF), Department of Polymers and Advanced Materials: Physics, Chemistry and Technology, University of the Basque Country UPV/EHU, Av. Tolosa 72, 20018 San Sebastián, Spain.*
[2] *IKERBASQUE, Basque Foundation for Science, Plaza de Euskadi 5, 48009.*

federico.calle@ehu.es

Keywords: platinum, generalized coordination numbers, coordination-activity plots, selectivity maps.

Introduction. Simultaneously, platinum is one of the scarcest and most promising electrocatalysts for several reactions of industrial and technological interest, which calls for the design of optimal Pt electrocatalysts. To do so, the most active sites for each reaction ought to be unambiguously determined and exploited. A computational tool for that purpose are "generalized coordination numbers" (GCNs).

Results and discussion. In my talk, I will first show that GCNs are able to describe adsorption-energy trends for unstrained Pt sites on extended surfaces and nanoparticles of different shapes and sizes with higher accuracy than conventional descriptors.[1, 2]

Subsequently, I will illustrate the use of "coordination-activity plots" based on GCNs to outline the geometric configuration of optimal Pt sites for three important reactions: oxygen reduction,[3, 4] CO oxidation,[5] and hydrogen evolution.[6] Besides, GCNs can be used to elaborate selectivity maps that help rationalize the intriguing selectivity of acetone electroreduction depending on the structure of Pt electrodes.[7]

Finally, I will show that GCNs and the plots based upon them can be extended to strained Pt electrodes,[8] Pt alloys[9] and other transition metal catalysts.[3, 10, 11]

Acknowledgments
I thank the organizers of Europacat 2023 for the invitation to deliver this talk, and the European federation of catalysis societies for the 2023 EFCATS Young Researcher Award.

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Europacat - EFCATS Best PhD Thesis Award

Pressure and temperature dependence of metallic zinc and partially reduced zinc oxide formation in copper-zinc-alumina catalysts – Limits of X-ray spectroscopy

A. Beck[1,2], M. Zabilskiy[3], M. A. Newton[2], O. Safonova[3], M. G. Willinger[2]*, J. A. van Bokhoven[2, 3]*

[1]University of California, Santa Barbara [2]ETH Zürich, [3]Paul Scherrer Institute

Rational catalyst design requires understanding of the structure of the catalyst in its working state. Such understanding is made possible by *in situ* and *operando* characterization. The wealth of new insights that these methods provide into catalysis has, at the same time, created numerous strong controversies and often studies on the same catalytic system have reported contradictory results. A prime example for such a system are Copper-zinc-alumina (CZA) catalysts:

CZA catalysts are the industrially-used formulation for methanol synthesis from carbon monoxide and carbon dioxide. The superior performance develops from synergies between its components. This important catalytic system has been intensively investigated, however, no comprehensive agreement has emerged as to the fundamental source of its high activity. One potential source of the disagreements is the considerable variation in pressure used in studies to understand a process that is industrially performed at pressures above 20 bar. Here, a systematic X-ray absorption spectroscopy study of the catalyst state during temperature-programmed reduction and under carbon dioxide hydrogenation is presented. The evolution of the catalyst over four orders of magnitude in pressure (1 mbar – 10 bar) shows how the state is defined by its environment [1,2,3]. In the light of the new systematic findings, existing controversies on the copper-zinc-alumina catalysts can be explained by considering the pressure regimes under which many previous studies have been conducted. Secondly, the talks shines light on the difficulty to differentiate between two central species using X-ray absorption spectroscopy, which debated for the reaction mechanism: the formation of a copper-zinc alloy containing metallic zinc and oxygen vacancy rich – partially reduced – zinc oxide.

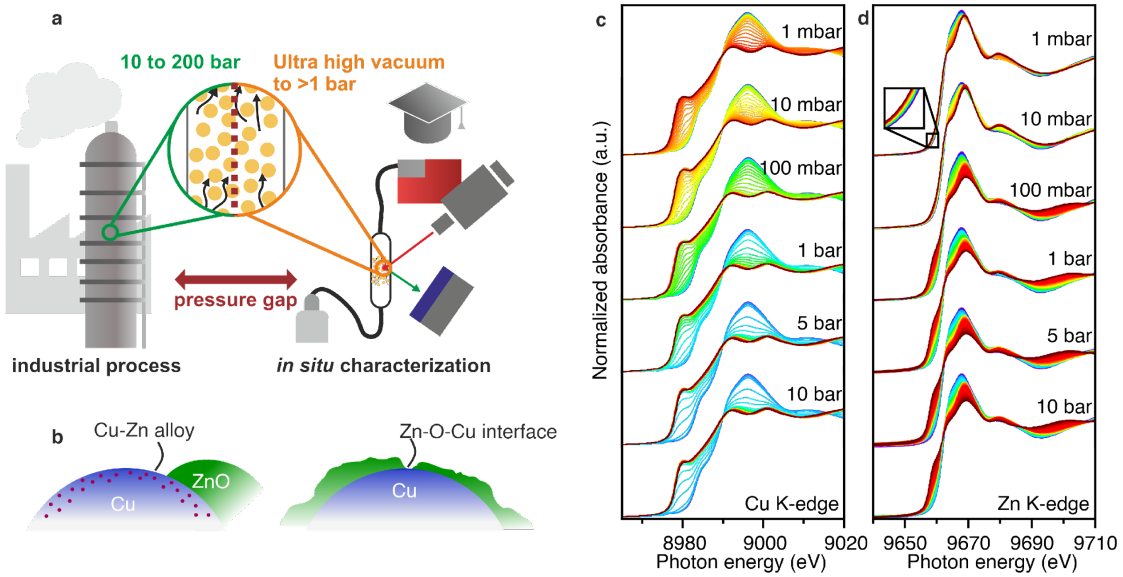

Figure 1: (a) The pressure gap existing between in situ characterization methods and conditions applied in industrial processes. (b) Proposals for the active site of copper-zinc catalysts. Cu (c) and Zn (d) K-edge XANES obtained during reduction under pressures of H_2 from 1 mbar to 10 bar.

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Biomass to chemicals and fuels

Sorption-enhanced steam reforming of toluene using multifunctional perovskite phase transition sorbents in a chemical looping scheme

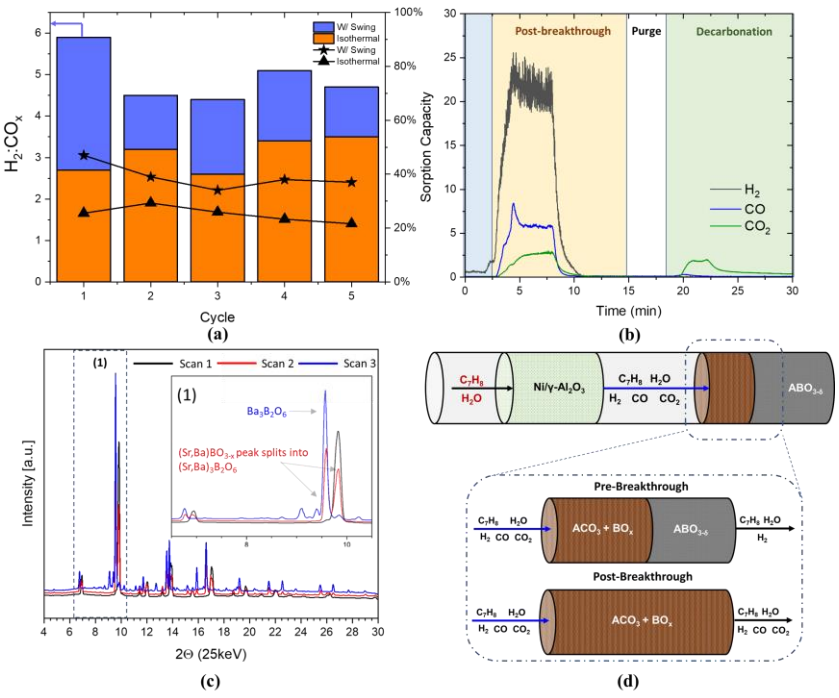
L. Brody[1], R. Cai[1], M. Rukh[1], K. Yang[1], M. Bekheet[2], S. Praetz[2],
C. Schlesiger[2], B. Kanngießer[2], R. Schomäcker[2], and F. Li[1*]

[1]*North Carolina State University, Raleigh, NC 27606 (USA)*
[2]*Technische Universität Berlin, Berlin 10623 (Germany)*
[*]*fli5@ncsu.edu*

Introduction. Sorption-enhanced steam reforming of toluene using catalytic CO_2 sorbents is a promising route to convert the aromatic tar compounds found in lignocellulosic biomass into hydrogen (H_2) or H_2-rich syngas. Commonly used sorbents are effective at capturing CO_2 initially but are prone to lose their sorption capacity (mole of CO_2/mole sorbent) over repeated cycles due to sintering at reaction temperatures. Herein, we present a demonstration of sorption-enhanced steam reforming of toluene using A- and B-site doped $Sr_{1-x}A'xFe_{1-y}B'_yO_{3-\delta}$ (A' = Ba, Ca; B' = Co) perovskites in a chemical looping scheme.

Experimental/methodology. The perovskite PTSs were synthesized using a modified Pechini method. Wet impregnation was used to introduce Ni to the surface. Redox catalysts' surface and bulk characterizations were conducted with XRD, XAS/XANES, XPS, and TGA. Reactive performance testing was conducted in a fixed bed quartz U-tube reactor containing 1.0 g of PTS (and 0.3 g of commercial NiO/ γ-Al_2O_3 when the sequential configuration was adopted) with liquid feeds controlled by programmable syringe pumps and gases delivered via a panel with automated cyclic valve switching. Mass spectrometry (MS) was employed to quantify conversion and sorption capacities. Additionally, two sorbents with different observed soprtion capacities were analyzed using synchrotron *in-situ* powder XRD analysis.

Results and discussion. We have extended the use of A-and B-site doped perovskite oxides to SESR of toluene under isothermal reaction conditions, both as stand-alone multifunctional catalytic sorbents as well as in a sequential packed bed configuration downstream of a commercial Ni-based catalyst (Ni/γ-Al_2O_3). We found that initial attempts to make an all-in-one multifunctional material via surface impregnation of 5-10 mol% Ni on the perovskite PTS succeeded in increasing activity for toluene conversion but is not a long-term solution due to undesirable Ni migration into the bulk as revealed by XRD analysis and Rietveld refinement. We solved this issue by adopting a sequential bed configuration with NiO/γ-Al_2O_3 upstream of $Sr_{0.25}Ba_{0.75}Fe_{0.375}Co_{0.625}O_{3-\delta}$ (SBFC-2635) and compared performance results for both isothermal and thermal swing experiments. While SESR was achieved isothermally for this material, the best results occurred when a 100 °C thermal swing was deployed, resulting in an average sorption capacity of ~38% and H_2:CO_x > 4.0 across five cycles. Additionally, the *in-situ* XRD patterns revealed a complex series of solid-state reactions that proceed once the sorbents are reduced and carbonated.



(a) Sequential bed results for isothermal and thermal swing; (b) MS profile detailing the chemical looping SESR cycle; (c) in-situ XRD patterns detailing rapid phase transitions during reduction/carbonation; and (d) a schematic of the sequential bed detailing pre-breakthrough phenomenon.

***Acknowledgments*.** This work was supported by the U.S. Department of Energy Office of Energy Efficiency & Renewable Energy (No. EE0008809) and US National Science Foundation (CBET- 1923468).

Vanadium-based catalysts for the sustainable production of formic acid from glucose

Débora Álvarez, Maria Isabel Dominguez Leal, Marcela Martínez T, S. Ivanova, Miguel Angel Centeno*

Instituto de Ciencias de Materiales de Sevilla, Centro mixto CSIC- Universidad de Sevilla, Avda. Americo Vespucio 49, 41092 Sevilla, Spain
centeno@icmse.csic.es

Keywords: formic acid, glucose, biomass

Introduction.

Hydrogen is the most promising energy vector able to participate in the green future in which fossil fuels are not involved. However, the difficulty and cost of its storage and transportation, limits its effective implantation. The use of formic acid as liquid organic hydrogen carrier can help to solve these drawbacks. The commercial industial production of formic acid is based on the CO reaction with methanol to produce methyl formate which is later hydrolyzed to formic acid, and CO is normally produced from coal or natural gas. Then, more sustainable and green routes for formic acid production are mandatory to be developed and one of them is the catalytic oxidation of residual biomass.

In this work, the catalytic performance of a series of V_2O_5/TiO_2 catalysts in the oxidation of glucose, as molecule representative of the cellulosic biomass, is evaluated.

Experimental/methodology.

V_2O_5/TiO_2 catalysts were prepared by wet impregnation and calcined at 450°C, starting from $VOSO_4$ and Titania P25. For the reaction, 400 mg of glucose dissolved in 20 mL water were introduced in presence of catalysts in a Parr reactor under pressure using O_2 as oxidant. The liquid products were analysed by HPLC. The influence of the catalyst charge (100-400 mg), time, temperature (100-170°C) and O_2 pressure (20-30 bar) was studied. All catalysts were characterized by TPR, XRD, UV-Vis, SEM, Raman and XPS.

Results and discussion.

All synthesized catalysts are able to produce formic acid as major liquid product. Fructose, produced by glucose isomerization, and traces of lactic, glycolic and acetic acids were also detected. Total glucose conversion and formic acid yields up to 45% were achieved when high reaction times and/or high temperatures were applied. However, incomplete carbon balances occur in these cases, pointing to the production of gaseous CO_2. The use of mild temperatures drives to lower formic acid yields (around 10%) but with total selectivity to formic acid. Concerning the catalysts, best results are obtained with those with the theoretical monolayer of vanadium species on the titania support, pointing out the importance of the nature of the surface vanadium species on the catalytic properties. Moreover, monolayer vanadium species are the most interacting with the titania surface, minimising the lixiviation of the active phase during the catalytic reaction.

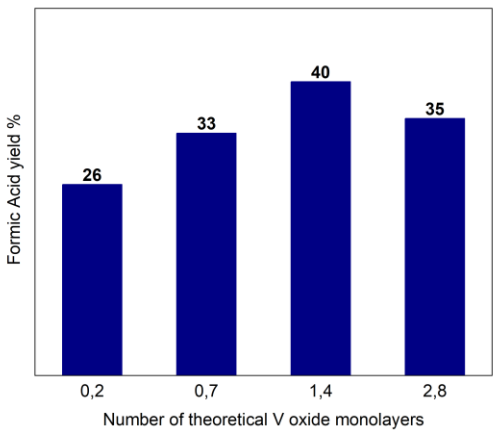


Figure 1. Formic acid Yield vs V content

Acknowledgments

Financial support was obtained from Spanish Ministerio de Ciencia e Innovación (MCIN/AEI/10.13039/501100011033/ FEDER Funds una manera de hacer Europa), Project PID2020-113809RB-C32.

Vanadium containing pillared clays as catalysts for acetaldehyde production by ethanol selective oxidation

E. Sabre[1,2], S. Casuscelli[1], A. Cánepa[1], V. Cortés Corberán[2*]

[1]*Centro de Investigación y Tecnología Química (CITeQ-UTN-CONICET), Córdoba, Argentina.*
[2] *Institute of Catalysis and Petroleumchemistry (ICP), CSIC, Marie Curie 2, 28049 Madrid, Spain.*
[*] *vcortes@icp.csic.es*

Keywords: acetaldehyde, ethanol, selective oxidation, pillared clay, vanadium catalysts.

Introduction. Acetaldehyde (AcH) is an industrially important solvent and an intermediate for the synthesis of a wide range of organic compounds [1]. Gas phase catalytic oxidation of ethanol (EtOH) from biomass by molecular oxygen (from air) is an economical and environmentally friendly process to produce it. Supported transition metal oxide catalysts, notably those of V, are effective for this reaction, but their perfomance depend on good oxide dispersion, that requires high specific surface area (SSA) supports. For instance, MCM-41 as support is efficient for this purpose [2], but its synthesis requires expensive reagents and generates wastes. Natural clays are an interesting alternative due to their low cost, great availability in nature, and ease to modify their properties by simple procedures. As the dispersion and nature of the supported V species depends on the nature of the support surface, we explored the use of titania pillaring to get efficient catalysts for this reaction, and investigated the effect of V content on their performance.

Experimental/methodology. The starting support (Ti-PILC) was synthetized from an Argentinian bentonite, that was purified and pillared by exchange with an acid $Ti(OBu)_4$ pillaring solution. Catalysts x%V/Ti-PILC (x=0.5-2 wt.% V) were prepared by wet impregnation, drying at 100ºC and calcination in air (450ºC, 3h) and characterized by BET, XRD, ICP-OES, Raman and DR UV-Vis spectroscopies and XPS methods. They were tested for EtOH selective oxidation in a fixed-bed continuous flow reactor (250-350ºC, W/F=1.55 g_{cat}.h/mol EtOH, EtOH:O_2=1) with on line analysis of reactants and products by GC.

Results and discussion. XRD showed the loss of regularity of the laminated structure of the Ti-PILC during catalyst synthesis and no peaks related to V_2O_5 phase, pointing to high V dispersion, which was confirmed by XPS. Though SSA of Ti-PILC decreased progresively with increasing V loading, all catalysts kept similar mesoporosity and high SSA (≥87 m^2/g). XPS spectra showed the V $2p_{3/2}$ peak for catalysts with V content >0.75 % wt. Its intensity increased with the V loading but with no shift the peak BE. The peak was composed by two contributions at 517.3 and 516.5 eV assigned to V^{5+} and V^{4+} respectively, with a ratio V^{5+}/V^{4+}>1 in all cases. All catalysts were active and very selective in EtOH oxidation. EtOH conversion increased with increasing V content and temperature, with a maximum of 87% at 350 ºC on 2%V/Ti-PILC, with 82% AcH selectivity. However, for all temperatures, productivity per V atom increased up to 1 wt.% V (equivalent to *ca.* 1 V atom/nm^2), with no change with the further increase of V content. Such V surface density is close to the reported value for the monolayer [3], which could indicate that most of the additional V content in the 2 wt.% V sample forms V oxide agglomerates, thus inhibiting their accessibility to the substrate.

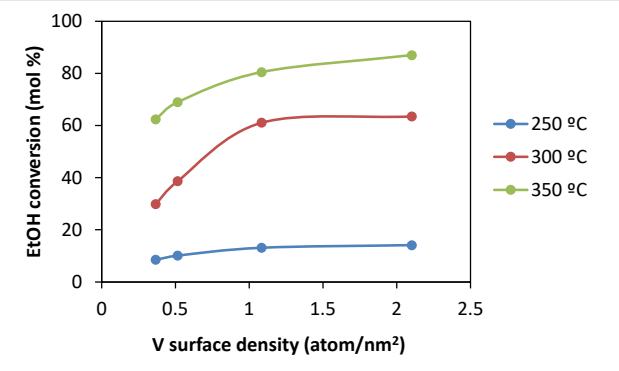


Figure 1. Effect of V surface density on EtOH conversion

Acknowledgments
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A showcase for comlexity of catalysis at liquid-solid interface: base-catalyzed isomerization of monosaccharides

Peter Drabo[1], Matthias Fischer[1], Valérie Toussaint[2], and Irina Delidovich[2*]
[1]*RWTH Aachen, Aachen, Germany*
[2]*TU Wien, Vienna, Austria*
[*]*irina.delidovich@tuwien.ac.at*

Keywords: glucose, fructose, solid base, leaching, salt effect, solvent

Transition from fossil feedstocks to renewable resources is accompanied by an increasing importance of heterogeneous catalysis in liquid phase. Design of heterogeneously catalyzed processes for liquid-phase transformations is hampered by the significantly less developed knowledge on processes at liquid-solid interfaces than understanding the widely used in petrochemistry solid-gas reactions. In this work, isomerization of D-glucose into D-fructose was considered focusing on influence of leached species, solvent, catalyst nature, and electrolytes onto reaction rate and selectivity.

The reactions were performed in batch reactors in the temperature range of 40 to 110 °C. Solid bases, such as MgO, CaO, SrO, $Ba(OH)_2$, Li_2CO_3, $MgCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$, Li_3PO_4, $Mg_3(PO_4)_2$, and Mg-Al hydrotalcites, were tested as catalysts. NaOH was applied as a soluble reference catalyst at constant pH values in the range of 9.5 to 11.5. Molecular amines, such as triethylamine or TBD, were tested under similar conditions for isomerization of fructose in various solvents, such as water, MeOH, DMF, and DMSO.

We explored contribution of leached OH^- species into catalysis of glucose-fructose isomerization by solid bases. The hydroxide ions are generated *in situ* through partial dissolution of bases with low solubility. Plotting initial rate of isomerization against concentration of OH^- in logarithmic scale suggested catalysis by leached OH^- species. Our studies indicate a limited applicability of a frequently used "filtration test" or a "contact test" to estimate contribution of homogeneous catalysis to the isomerization catalyzed by solid bases. Kinetic studies coupled with monitoring the concentrations of leached OH^- and metal ions proved to be significantly more informative. Interestingly, catalyst composition influences the product selectivity. For instance, improved selectivity for fructose was observed for catalysis by Mg-Al hydrotalcites or $MgCO_3$.[1, 2]

We observed a significant acceleration of the isomerization rate, up to x6, in the presence of soluble neutral salts, such as NaCl or Na_2SO_4. The salt effect was observed in the presence of soluble base NaOH as well as solid catalysts Li_3PO_4, MgO, and Mg-Al hydrotalcites. We found out that the observed salt effect is caused by a dependency of a thermodynamic acidity constant of glucose on concentration of electrolytes.[3]

Solvent nature impacts isomerization selectivity. Thus, conversion of fructose in the presence of amines gives rise to glucose in water and to allulose in DMSO or DMF. The selectivities are in good correlation with the concentrations of the tautomers, suggesting fructopyranose as substrate for formation of glucose and fructofuranose as substrate for allulose. Thus, changes in tautomeric equilibrium for different solvents result in change of selectivities.[4]

In summary, our results on base-catalyzed isomerization of glucose and fructose suggest that catalysis on the liquid-solid interface presents a complex phenomenon with contributions of catalyst nature, leached species, solvent, and electrolytes.[5]

Acknowledgments
We thank the DFG (Project 397970309) and the BMEL (Project 281A200316) for the financial support.

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Efficient conversion of polysaccharides to glucose in water using a heterogeneous ionic polymer catalyst

K. A. Abhyankar[1], R. J. Somerville[1], F. Fadei Tirani[1], Z. Fei[1] and P. J. Dyson[1]*

[1]*Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland*

Keywords: biomass valorisation, polysaccharide hydrolysis, ionic polymer, solid acid

Introduction. Catalytic polysaccharide hydrolysis is a key step in the valorisation of cellulosic and starchy biomass, as glucose is a key intermediate in potential biorefineries[1] for the production of fuels and platform chemicals (e.g. dimethylfuran, levulinic acid, γ-valerolactone)[2]. Carrying out this hydrolysis with heterogeneous catalysis in water is desirable as it improves catalyst separation and avoids organic solvents. We report the systematic design of vinylimidazolium salts containing pendant carboxylic acid groups and their use in cellulose and starch depolymerisation in water. The most promising vinylimidazolium salt was polymerised resulting in a cross-linked weakly acidic polymer network that heterogeneously catalyses starch depolymerisation to glucose in water.

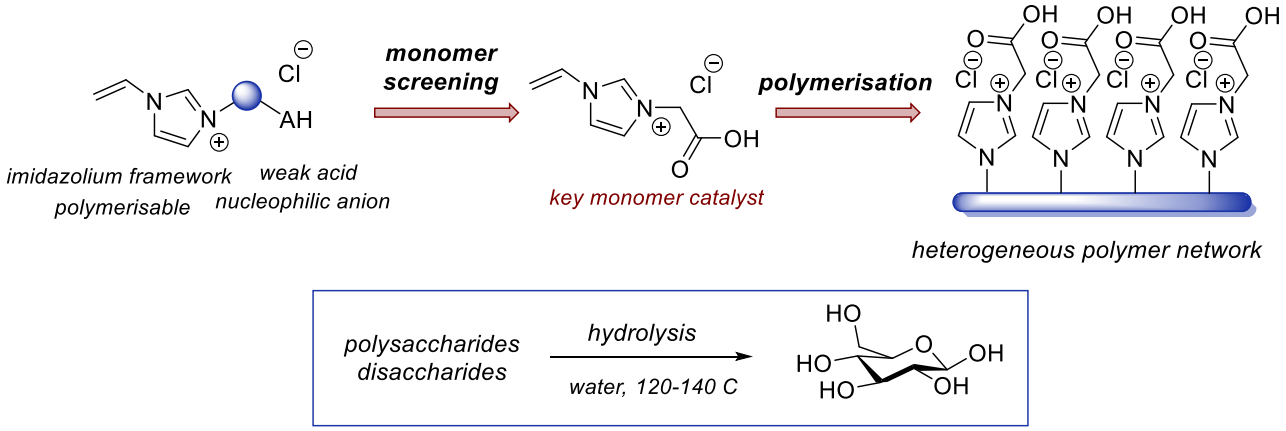

Figure 1: Design of weakly acidic ionic polymer for polysaccharide hydrolyis

Experimental/methodology. The series of vinylimidazolium monomers was screened against the model compounds cellobiose and maltose (which are homogeneous models of cellulose and starch, respectively). Glucose was quantified by HPLC-RID. The most effective monomer was next tested against polysaccharides cellulose and starch. This monomer was then polymerised to create a cross-linked insoluble acidic polymer network for the heterogeneous cleavage of saccharides. The heterogeneity of the polymer catalyst and the hydrothermal stability of the polymer was investigated and humins deposition onto the polymer surface proposed as a possible catalyst poisoning pathway. Monomer catalysts were characterised by NMR spectroscopy, mass spectrometry and X-ray crystallography. The polymer catalyst was catalysed by solid state NMR spectroscopy, differential scanning calorimetry, and thermogravimetric analysis.

Results and discussion. With the most active monomer, good yields of glucose were obtained from model saccharides, cellulose, and potato starch. Subsequent polymerisation resulted in a heterogeneous ionic polymer catalyst which was active for the conversion of model saccharides and potato starch to glucose in water. Gratifyingly, the yields obtained with the polymer catalyst mirrored those obtained with the monomer catalyst in most cases and were obtained in water at relatively mild temperatures (120 –140 °C). Importantly, catalysis with the polymer network was found to be heterogeneous and the catalyst remains active even at low (1:10 catalyst:potato starch, by mass) loadings.

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Enhanced Reductive Catalytic Fractionation of raw lignocellulosic biomasses with magnetic recyclable catalyst

F. Bugli[1], T. Tabanelli[1*], D. Lorito[2], M. Sgarzi[3], F. Cavani[1]

[1] *Alma Mater Studiorum University of Bologna, Department of Industrial Chemistry "Toso Montanari", viale del Risorgimento 4, 40136 Bologna (BO)*

[2]*Eni Renewable, New Energy and Material Science Research Center (DE-R&D), Via Fauser 4, 28100 Novara (NO)*

[3] *Ca' Foscari University of Venice, Department of Molecular Sciences and Nanosystems, Via Torino, 155 30172 Venezia Mestre (VE)*

[*]*tommaso.tabanelli@unibo.it*

Keywords: lignocellulose fractionation, lignin depolymerization, RCF, magnetic catalyst

Introduction. Fractionation of lignocellulosic biomasses is an essential step for biorefinery strategies to isolate and fully exploit cellulose, hemicellulose and lignin for the production of materials, fuels and chemicals[1]. Conventional pre-treatments usually involve loss of mass or functionalities due to the different effects of process conditions on different structural components. In particular, lignin faces irreversible structural modification because of the lability of ether linkages (C-O-C), and re-condensation reactions of unstable intermediates (i.e. aldehydes) forming novel C-C bonds which confer higher recalcitrance to the "processed" lignin structure leaving few prospective of valorisation[2]. One of the most promising strategies aimed to the valorisation of the lignin fraction is based on the extraction, depolymerisation and simultaneous stabilisation of lignin fragments towards the production of low molecular weight lignin oil through the so called Reductive Catalytic Fractionation (RCF)[3]. RCF is a catalyst dependant process capable of producing phenolic compounds and lignin oils while preserving the carbohydratic pulp in the presence of a reducing agent, generally hydrogen[4]. Noble metal catalysts supported over active carbons were found to be active for the target process; however, one major issue, often underestimated, is represented by the inefficient catalyst recovery from the fibrous cellulose solid pulp which limits catalyst recyclability thus impacting the economic sustainability of the entire process[5].

Experimental/methodology. Catalytic tests were performed in a batch reactor (autoclave) loading either raw poplar wood or an actual urban pruning waste residue, with the desired amount of catalyst and a binary water/1-butanol mixture already known to be efficient for the extraction of lignin as well as for the simplification of the downstream separation procedures (i.e. hemicellulose polyols retained in water phase while lignin derived products are readily solubilized in butanol)[6]. An innovative Ru/γ-Fe_2O_3 was synthesized via Incipient Wetness Impregnation of a commercial magnetite and calcination at 400°C.

Results and discussion. Considering all the problems described in the introduction section, we developed a novel magnetic catalyst based on 5wt% Ru/γ-Fe_2O_3 active for RCF and easily recoverable through the application of an external magnetic field with high recovery yield (around 90%). In particular, we focus on the comparison between our catalytic system and a commercial 5wt% Ru/C catalyst in terms of delignification of cellulose, lignin oil yield and catalyst recovery. The magnetic catalyst is characterized by lower surface area compared to Ru/C, this feature probably affecting Ru dispersion finally limiting lignin depolymerisation efficiency to monomers (i.e. phenolics), nonetheless we were able to get both higher cellulose delignification and lignin oil yield. Furthermore, preliminary recyclability test have proven the stability of our catalyst for at least 3 cycles of reaction. This catalyst shows great potential thanks to its good stability and recyclability, its ability to produce high quality cellulose pulp together with relatively low MW lignin oil without affecting the economic sustainability of the process. Future work will be devoted to the improvement of the phenolic monomers yield as well.

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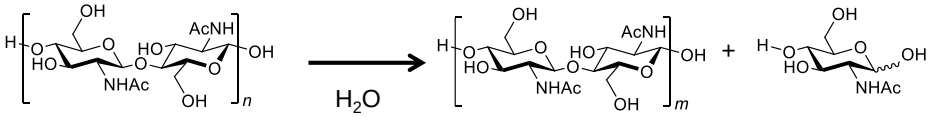
Selective Synthesis of Oligosaccharides by Depolymerization of Chitin over a Carbon Catalyst

Atshushi Fukuoka[1*], Hirokazu Kobayashi[2]

[1]*Institute for Catalysis, Hokkaido University, Sapporo, 001-0021, Japan*
[2]*Komaba Institute for Science, The University of Tokyo, Tokyo, 153-8902, Japan*
[*]*fukuoka@cat.hokudai.ac.jp*

Keywords: chitin, oligosaccharides, carbon catalyst, depolymerization, hydrolysis

Introduction. Chitin-oligosaccharides, trimer to hexamer of *N*-acetylglucosamine (NAG), can activate the immune systems of plants as biostimulants, and the oligosaccharides may facilitate the growth of plants. However, the oligosaccharides are in short supply, because their selective synthesis is difficult. We have been studying the depolymerization of chitin to NAG and conversion of NAG to organonitrogen compounds [1-4]. Herein, we demonstrate the selective synthesis of chitin-oligosaccharides from chitin over a carbon-based solid catalyst named AC-Air (Equation). Using a planetary ball-mill, weak acid sites on the catalyst show high activity toward the hydrolysis of chitin to the oligosaccharides [5].



Experimental/methodology. AC-Air was prepared by heating steam-activated carbon (AC) in air at 425 °C for 10 h. Chitin powder was milled with a catalyst for 12 h with alumina balls in an alumina pot at 500 rpm by a planetary mill. After the milling process, the products were analyzed by HPLC.

Results and discussion. We observed high activity of AC-Air in the hydrolysis of chitin in a planetary milling system, in which the selectivity for the chitin-oligosaccharides reached over 90% (Table 1). As shown in entry 1, the non-catalytic reaction gave low yields of NAG and the oligosaccharides in 12 h. AC-Air increased yields of NAG to 2.8 %C and oligosaccharides to 32 %C (entry 2). The selectivity for oligosaccharides was as high as 94%. The oligomer fraction contained not only dimer (4.7 %C) but also larger oligomers (trimer 5.9%C, tetramer 6.5 %C, pentamer 5.2 %C, hexamer and larger 9.7%C). Notably, this reaction produced no acetic acid, indicating no hydrolysis of the amide groups in chitin. This feature is in sharp contrast to aqueous-phase reactions that hydrolyze both glycosidic and amide bonds. The yield of oligosaccharides increased to 66 %C by extending the reaction time to 48 h, while maintaining 92% selectivity (entry 3). The catalyst was reusable after washing with dilute HCl to remove the adsorbed amines originally contained in chitin. For comparison, we performed a mechanocatalytic hydrolysis of chitin with H_2SO_4 (entry 4). This reaction gave a 95% solubilization ratio and 62 %C yield of oligomers, but the selectivity for oligomers was only 65%. The by-product formation was verified by NMR analysis. We analyzed the time course of the mechanocatalytic hydrolysis, and applied Monte Carlo simulations that virtually hydrolyzed a chitin molecule. These results show that AC-Air can cleave glycosidic bonds of chitin molecules without influence of the molecular size. Consequently, the mechanocatalytic system can reduce the successive hydrolysis of small oligomers, thus giving a high yield and selectivity of oligosaccharides.

Table 1. Mechanocatalytic hydrolysis of chitin with solid catalysts.

Entry	Catalyst	Yield of products /%C		Solubilization ratio /%
		NAG	Oligomers (Selectivity /%)	
1	-	0.1	1.2 (15)	8.2
2	AC-Air	2.8	32 (94)	34
3	AC-Air	8.3	66 (92)	72
4	H_2SO_4	7.3	66 (65)	95

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Catalytic screening for microalgal bio-oil hydroconversion

B. Da Costa Magalhães[1], P. Afanasiev[1], D. Laurenti[1]*, C. Geantet[1]

[1]*IRCELYON, CNRS-Univ. Lyon 1, UMR 5256, Villeurbanne, France*
[*]*dorothee.laurenti@ircelyon.univ-lyon1.fr*

Keywords: Catalytic upgrading - Biofuel – Ni(Mo)W Sulfide – NiMo Nitride – Ni Phosphide - GC×GC

Introduction

Global energy demand and environmental concerns about limiting CO_2 emissions and carbon footprint have been growing recently. In this context, fuel production from renewable resources has become a priority, especially for aviation. Among sustainable bio-resources, microalgae represent an attractive alternative to provide carbon molecules due to their fast-growing rate and the potential high lipid content. In addition, microalgae can be easily transformed into oil by the hydrothermal liquefaction (HTL) process. The microalgal oils still contain a large quantity of O-, N- or S- compounds that have to be reduced to be used as fuel. Particularly, the main components of HTL microalgal oil are the C16-C18 fatty acids issued from the lipids conversion during the HTL process. Those acids, in addition to other components like amides, alkenes, esters, or alcohols are not compatible with transport fuels and need to be upgraded to hydrocarbons. In this work, we propose catalytic upgrading, including deoxygenation, denitrogenation, and desulfurization of an HTL oil obtained from *Chlorella vulgaris* microalga [1] with various supported catalysts having hydroconversion ability.

Experimental/methodology. Supported catalysts (Ni_2P/Al_2O_3, Ni_2P/SiO_2, and $NiMoN/Al_2O_3$) were prepared on the various oxide supports following published works [2,3] and compared to benchmark sulfided catalysts (NiW/Al_2O_3, $NiMo/Al_2O_3$, $NiWS/SiO_2$-Al_2O_3). HTL oil of *C. vulgaris* was provided by CEA Liten. The catalytic tests were performed in a batch reactor under H_2 pressure. Typically, algal oil (3 g) was mixed with 0.6 g of supported catalyst in 25 g of heptane and heated under 1 MPa of H_2. When reaching the reaction temperature (375°C), the reactor was filled with H_2 to reach 10 MPa pressure. Afterward, the mixture was filtered to recover the catalyst, and the heptane was removed by evaporation.

Results and discussion. The main compounds in *C. vulgaris* HTL oil were the C16 (9.3 wt%) and C18 (24.2 wt%) fatty acids. During the upgrading, they were converted readily to the corresponding alkanes by hydrodeoxygenation (HDO) or decarboxylation/decarbonylation (DCO) [4]. The refractory compounds are fatty amides, nitriles, and the various heterocyclic nitrogen molecules coming from proteins. Supported Ni_2P catalysts promoted the DCO route, while $NiMoN/Al_2O_3$ promoted the HDO pathway. Among sulfide catalysts, $NiWS/SiO_2$-Al_2O_3 showed low performances, probably due to the inhibition of acid sites by the nitrogen compounds of the bio-oil. Alumina-supported NiWS catalyst was the most performant solid for the studied reaction, producing a hydrotreated oil with the best higher heating value (HHV), the lowest aromaticity degree, and the lowest average molar mass. The most refractory remaining are cyclic nitrogen compounds such as indoles, pyrroles, and carbazoles. The biofuels obtained with the various catalysts fall mainly in the diesel and jet-fuel ranges as observed by SimDist. For instance, for $NiWS/Al_2O_3$ catalyst, 66 wt% of the liquid is recoverable as traditional fuels. Moreover, with this catalyst, a higher reaction temperature (400°C) allowed increasing the jet fuel and diesel fraction, reaching a total of 80 wt%. The screening of catalysts has thus revealed the alumina-supported NiWS catalysts as a robust and performant system to upgrade micro-algal oils into biofuels. The heavier fraction might be hydrocracked in a second step to obtain an even higher light fraction yield.

Acknowledgments

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Ruthenium ion catalysed C-C bond cleavage in lignin model compounds - Towards lignin depolymerisation.

Meenakshisundaram Sankar[1*], Susana Guadix-Montero[1], Mala A. Sainn[1], Graham Forsythe[2], Gary N. Sheldrake[2], David Willock[1]

[1] *Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, United Kingdom*

[2] *School of Chemistry and Chemical Engineering, David Keir Building, Stranmillis Road, Queens University Belfast, Belfast BT9 5AG, Northern Ireland, United Kingdom.*

** Meenakshisundaram Sankar: sankar@cardiff.ac.uk*

Lignin, one of the three major components of lignocellulosic biomass, is a cross-linked amorphous phenolic biopolymer that gives plants their structural strength and shape. It contains highly functionalised aromatic units that makes them a potential renewable and sustainable feedstock to produce aromatics and has the potential to replace fossil-fuel based feedstock in producing fuel and base chemicals.[1] To valorise lignin, it is crucial to break both the C – O and C – C inter unit linkages, to make biorefining economically viable and sustainable. Depending on the biomass, 25-34% of the inter-unit linkages are C – C linkages and they are more recalcitrant compared to the C – O inter-unit linkages. The bond dissociation energies of C – C and C – O linkages are 226 – 494 kJ mol^{-1} and 209 – 348 kJ mol^{-1} respectively. Consequently, most of the reported valorisation strategies focus on the cleavage of C – O linkages resulting into *ca.* 60 wt.% of un-valorised lignin fraction having predominantly C – C inter-unit linkages. Here we employ the ruthenium ion catalyzed oxidation (RICO) for the oxidative cleavage of the most recalcitrant C – C inter unit linkages found in lignin: the 5-5' bond linking two aromatic rings (BDE 481 – 494 kJ mol^{-1}). We use biphenyl and custom made model hemaxer for this study [Figures 1 & 2].[2] All the reactions were carried out in a glass flask at 295 K using a mixture of water and acetonitrile as the solvent. $RuCl_3$ was used as the Ru source and $NaIO_4$ was used as the oxidant and RuO_4 was generated *in situ* during this oxidative depolymerisation reaction. Qualitative and quantitative analyses of the reaction mixture were done using ^{1}H, ^{13}C NMR spectroscopy methods along with GC-MS and Gel Permeation Chromatographic (GPC) methods. Advanced 2D NMR spectroscopic methods such as HSQC, HMBC and ^{31}P NMR spectroscopy after phosphitylation of the mixture were employed to quantitatively analyse the breaking of the β-5, 5-5' [Figure 2] and β-O-4 linkages and to identify the products. Density functional theory (DFT) with the hybrid B3LYP functionals were used to calculate energies of intermediates and transition states using the Gaussian09 package.

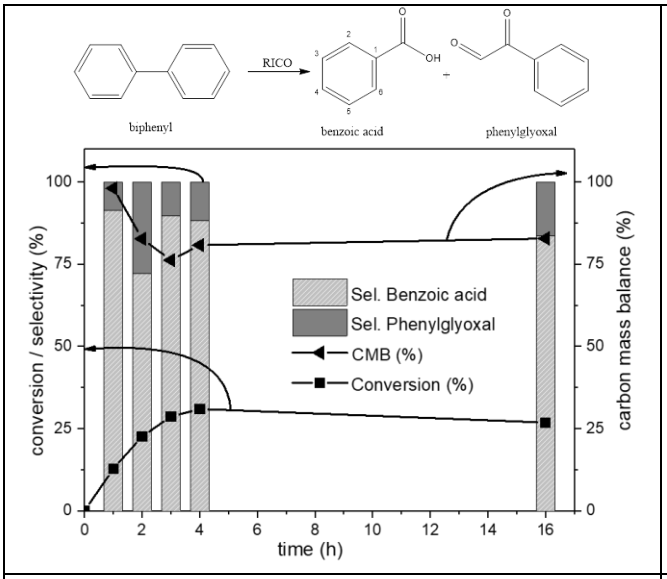

Figure 1. *Time online of the RICO reaction for biphenyl with a molar ratio of substrate, oxidant, and catalyst of [1:2.67:0.03]. Biphenyl conversion (-■-), carbon mass balance (-◄-), the selectivity of benzoic acid ( ) and selectivity of phenylglyoxal ( ). 75 mg Biphenyl, 280 mg NaIO4 and 0.23 mL of $RuCl_3xH_2O$ stock solution. 30 mL of reaction solvent mixture of 2:1 Acetonitrile-deionise water, at 22 °C, 1 atm.*

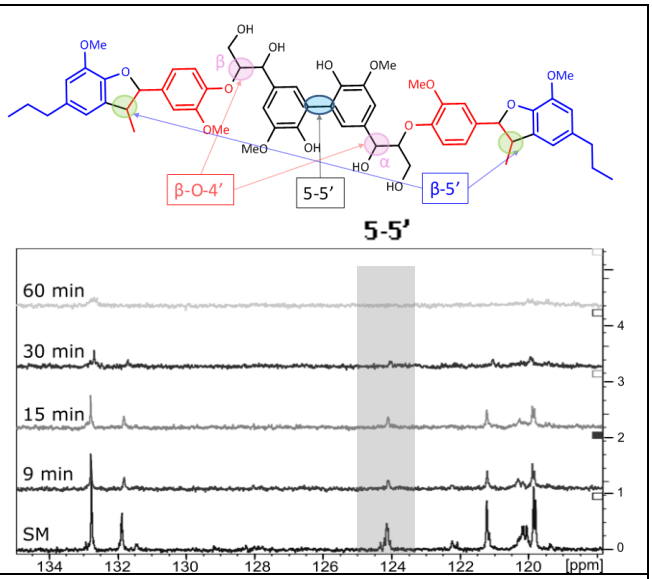

Figure 2. *Structure of the model hexamer used for the oxidative depolymerisation reaction (top). Comparison of ^{13}C NMR spectra : From the bottom to the top - Starting Material (SM), products obtained after 9 min, 15 min, 30 min and 1 h of RICO reaction (bottom).*

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Relationship between number and strength of acid-base catalytic sites and their selectivity in isopropanol dehydration reaction

L.Silvester[1], G. Postole[*,1], S. Segondy[1], A. Auroux[1], J.-L. Dubois[2]
[1]*Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, 69626, Villeurbanne, France*
[2]*Arkema France, 420 Rue d'Estienne d'Orves, 92705 Colombes, France*
[*]*E-mail address: georgeta.postole@ircelyon.univ-lyon1.fr*

Keywords: NH_3/SO_2 adsorption microcalorimetry, acid-base sites, isopropanol dehydration, propylene

Introduction.

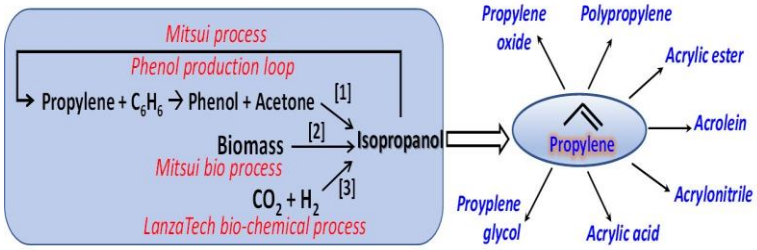

Figure 1. Novel isopropanol production routes and the commercial interest towards isopropanol dehydration to propylene

Propylene (PEN) is considered as a versatile building block in most of the petrochemical industries to produce valuable chemical intermediates such as polypropylene, acrylonitrile, acrolein, acrylic acid etc. Currently, PEN is primarily produced as a by-product during the ethylene in the naphtha steam crackers and fluid catalytic cracking (FCC) units, but also through MTO/MTP and metathesis. Considering the recent trends in the production of isopropanol using environmentally friendly processes, for *e.g.*, Mitsui and LanzaTech processes, the commercial propylene production from isopropanol dehydration is gaining more attention (see figure 1) [1-3]. Isopropanol (IPA) dehydration to propylene (PEN) is not new to the catalysis world but the formation of side products, particularly, di-isopropyl ether (DIPE) and acetone makes it still a tricky reaction that requires very fine catalysts tuning/selection criteria (amount and distribution of the active sites) in attaining polymer grade PEN.

Results and discussion. In this study, the adsorption microcalorimetry investigation using NH_3 and SO_2 probe molecules helped us to finely tune and classify different solids such as Alumina, Silica Alumina, Bentonite (clay type) etc. based on their acid-base properties (figure 2). The adsorption isotherms and their corresponding differential heats obtained for some of the selected solids revealed their entirely different acid/base behavior, *i.e.*, the alumina exhibiting amphoteric nature, the silica-alumina being predominantly acid with very low basicity and the bentonite possessing only acid sites (figure 2). The IPA dehydration was then performed to study the reaction kinetics and further to draw correlations between catalytic sites and reaction products. Correlations have been established between the ratio of acid to basic sites and the PEN/acetone formation. These correlations helped us to further optimize the catalysts and reaction conditions for attaining very high PEN selectivity. The high temperature and low pressures favored PEN while low temperature and high pressure resulted in the by-product DIPE [4]. However, too much increase in the temperature can result in the issues such as PEN polymerization and coking. Employing sufficiently high gas linear velocity and large pore catalysts can avoid the problems due to diffusion limitations [4].

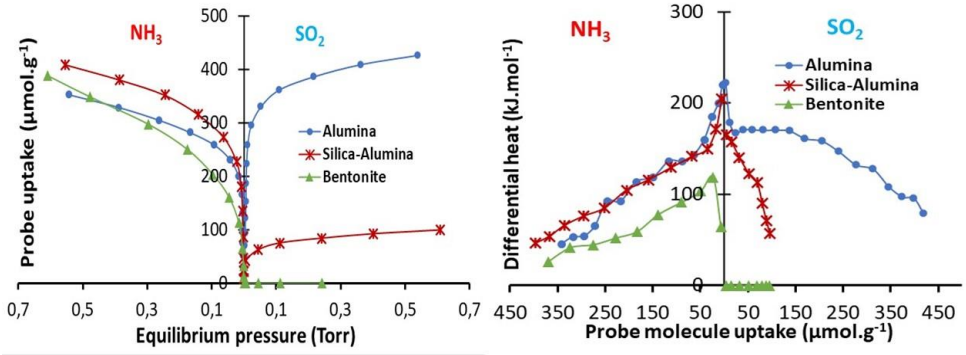

Figure 2. Adsorption isotherms & different heats from calorimetry

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Furfural manufacture at high yield

J.-P. Lange
Shell Global Solutions International B.V., Amsterdam, The Netherlands
Sustainable Process Technology, University of Twente, Enschede, The Netherlands
e-mail: jean-paul.lange@shell.com

Introduction.
To mitigate climate change and decrease society's reliance on fossil resources, the industry must develop new routes to produce fuels and chemicals from renewable carbon resources. Some of them include furfural as platform molecule to valorize the ~20 wt.% xylose present in hard wood and grasses. Present furfural production processes valorize only half the xylose and use the rest of the biomass (85-90wt%) as energy source for powering the process. This lecture will present novel furfural manufacturing routes that promise high biomass utilization by extracting the xylose for furfural production and leaving the rest for alternative valorization options.

Results.
A first approach integrates biomass fractionation with biphasic xylose dehydration and recycling of the acidic aqueous phase [1]. The resulting furfural yield of ~70 mol% (based on xylose) can further be lifted to ~90 mol% by applying microwave heating and adjusting the medium composition [2].

A second approach integrates the biomass fractionation with novel two-step processes to produce furfural with 90% yield and low energy demand. This is achieved by selectively extracting the dilute xylose as boronate ester and, subsequently, dehydrating it to furfural either in a water-organic homogeneous phase or under biphasic saline conditions (Fig. 1, [3,4]). These process concepts are designed for efficient recycling of all components, i.e., the boronic acids, the organic solvents and/or the saline solution. Dedicated kinetic study assigned the high furfural selectivity to the balance between the rates of boronate hydrolysis and xylose dehydration [5].

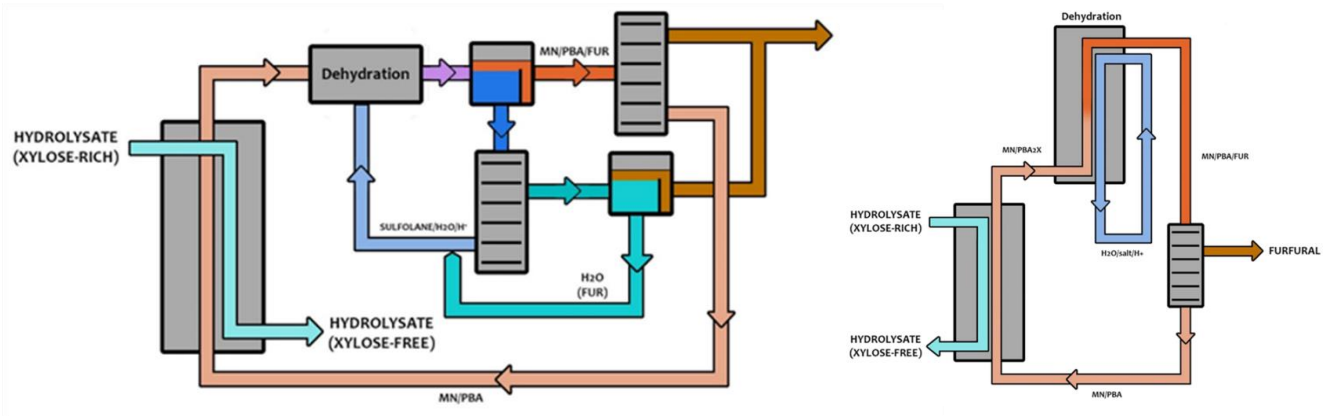

Figure 1. Process concepts for converting diluted Xylose hydrolysate to furfural with 90% selectivity, via extraction as boronate ester and subsequent dehydration in monophasic medium (left, [3]) or in biphasic saline medium (right, [4]).

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This work would not have been possible without the outstanding contribution of many colleagues, particularly J. Chheda, E. Cabrera, and J. Flores (Shell) as well as L. Ricciardi, W. Verboom, and J. Huskens (U. Twente).

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Tunable Ru-Ni catalysts with controlled particle size for 5-hydroxymethylfurfural hydrodeoxygenation

Agnieszka Ruppert[1*], Magdalena Brzezinska[1,2], Nicolas Keller[2]

[1] *Institute of General and Ecological Chemistry Faculty of Chemistry Łódź University of Technology ul. Żeromskiego 116 90-924 Łódź (Poland)*
[2] *Institut de Chimie et Procedes pour l'Energie l'Environnement et la Sante (ICPEES) CNRS, University of Strasbourg 25 rue Becquerel 67087, Strasbourg (France)*
[*] *Corresponding Author's E-mail address: agnieszka.ruppert@p.lodz.pl*

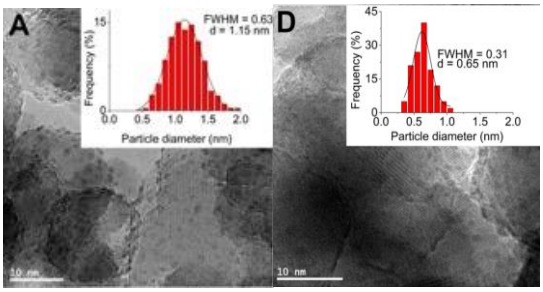
Introduction. 5-hydroxymethylfurfural (HMF) derived from the lignocellulosic biomass feedstock is considered as a versatile platform molecule that can be converted into a wide span of desirable chemicals ranging from fuels to plastics. Among them, 2,5-dimethylfuran (DMF) and 2,5-dimethyltetrahydrofuran (DMTHF) are pivotal molecules of high value, with applications as biofuels or biofuel additives.

One of the most efficient metals in the hydrogenation and hydrogenolysis of many biomass-derived oxygenates is ruthenium, mainly owing to its outstanding performance that rely on the decrease of the energetic span of the reaction pathway in the presence of a protic solvent [1]. Its very high activity is however an obstacle for obtaining high selectivity, as it is a challenge to tune its properties in order to avoid overhydrogenation reactions or other secondary reactions.

Methodology. The TiO_2 supported Ru and Ru-Ni catalysts were prepared according to a solar light photon-assisted synthesis method [2] over a broad range of Ru:Ni ratios. Catalysts were characterized by numerous surface and bulk techniques including HRTEM, ToF-SIMS, XPS, XRD, TPR. Catalysts were tested in the liquid phase 5-hydroxymethylfurfural hydrodeoxygenation (30 bar H_2 in 160°C for 4 h).

Results and discussion.

Regardless of the Ru:Ni ratio in the bimetallic Ru-Ni/TiO_2 catalyst, the photon-assisted synthesis leads to small size Ru nanoparticles homogeneously dispersed at the surface of the TiO_2 support with a narrow particle size distribution, and no aggregates were observed. What is more, the presence of nickel favoured the reduction of the mean Ru nanoparticle size, that decreased from 1.1 nm for the monometallic Ru catalyst down to 0.6 nm for the bimetallic Ru-Ni catalysts. The Ru/TiO_2 reference catalyst led to moderate performances, with a HMF conversion and a DMF selectivity of 46% and 72%, respectively. We evidenced that the increase of the Ni/Ru bulk ratio favoured the HMF conversion, that reached 100% for a Ni/Ru molar ratio of 1.5. By contrast, the DMF selectivity pattern exhibited a volcano-like shape, with a maximum selectivity of 96% being achieved for a Ni/Ru molar ratio of 1.0. Thanks to this novel sustainable method, highly selective and stable Ru-Ni catalysts have been developed, with an activity that can be easily optimized through the tuning of the Ru:Ni ratio.



TEM images of the A) 5%Ru/TiO_2 and D) 5%Ru-5%Ni/TiO_2

Acknowledgments

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Design of Aluminum Phosphate Catalysts for Selective Valorization of Biomass-derived Furfural

W. Fang[1], A. Riisager[1*]

[1]*Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, Kgs. Lyngby, Denmark*
[*]*ar@kemi.dtu.dk*

Introduction. Furfural (FF) is a lignocellulosic biomass-derived precursor molecule, which can be converted into numerous value-added chemicals [1]. The aldehyde group of FF can undergo important transformations, including reduction, reductive etherification, acetalization, and aldol condensation (Figure 1). Aluminum phosphate (APO-5) is a zeotype material possessing an AFI structure with 12-membered rings with large pore size (7.3 Å) [2], which is suitable for conversion of FF [3]. Catalytically active sites (acidic sites) can be created in the theoretically neutral APO-5 structure by different routes and the resulting catalysts applied for various acid-catalysed reactions.

Experimental/methodology. APO-5 catalysts with different Al/P ratios were prepared by hydrothermal synthesis. Alkali earth metals (AEMs)-loaded and Zr-doped APO-5 catalysts were prepared by corresponding impregnation and isomorphous substitution.

Results and discussion Highly selective and durable APO-5 catalysts were designed for various valorization reactions of FF at mild conditions (i.e. 120-150 °C). As shown in Table 1, weakly acidic APO-5 (Al/P = 1) showed excellent catalytic performance for the acetalization of FF with ethylene glycol to obtain **1** due to co-catalysis of adsorptive and acidic sites [4]. More acidic APO-5 (Al/P = 1.5) catalyzed both catalytic transfer hydrogenation and subsequent etherification of FF in 2-propanol with good yield of **2** besides ring opening and hydrogenation products [5]. Introduction of alkali-earth metal oxides, e.g. calcium oxide, in Ca/APO-5 (Al/P = 1.5) allowed to modify the acidity and basicity of the catalyst, which improved the selectivity to hydrogenation product **3** and further suppressed side reactions, e.g. etherification, acetalization and ring opening reaction [5]. Furthermore, introduction of Zr into the framework enhanced the adsorption for C=O bond and created suitable acidic and basic sites, promoting the aldol condensation of FF with cyclohexanone to obtain **4** [6]. Notably, all the APO-5 catalysts also displayed high catalytic activity in the conversion of other bio-derived aldehydes.

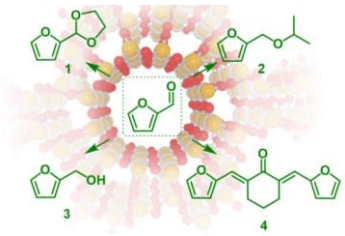

Figure 1. Furfural valorization

Table 1. Furfural valorization with APO-5 catalysts

Catalyst	Acidity (mmol/g)	FF Conv. (%)	Product Yield (%)
APO-5 (Al/P = 1)	0.001	97	96 (**1**)
APO-5 (Al/P = 1.5)	0.40	95	55 (**2**)
Ca/APO-5 (Al/P = 1.5)	0.25	97	90 (**3**)
ZrAPO-5 (Zr/Al/P = 0.2/1/1)	0.52	99	79 (**4**)

Overall, the work demonstrates a simple approach to design heterogeneous APO-5 catalyst systems for the efficient and highly selective valorization of biomass-derived FF to value-added chemicals.

Acknowledgments

The authors thank the Department of Chemistry, Technical University of Denmark for support. W.F. acknowledges the China Scholarship Council for awarding a scholarship.

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Beyond γ-valerolactone: from levulinates to C5 and C7 esters through innovative continuous-flow processes in the gas phase

T. Tabanelli[1,2*], L. Visentin[1], A. Ventimiglia[1], M. Berti[1], N. Dimitratos[1,2], I. Rivalta[1], S. Albonetti[1,2], L. Ardemani[3], N. Scotti[3] and F. Cavani[1,2]

[1] *Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy*
[2]*Center for Chemical Catalysis-C3, Università di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy*
[3]*CNR Institute of Chemical Sciences and Technologies "G. Natta", Milano, Italy*
[*]*tommaso.tabanelli@unibo.it*

Keywords: catalytic transfer hydrogenation, alkyl levulinates, ethanol, zirconia, continuos-flow, gas-phase

Introduction. Levulinic acid (LA) and its esters (LE) are important, polyfunctional molecules that can be obtained from lignocellulosic biomass through hydrolysis or alcoholysis respectively. The most applied strategy for their valorization is the chemical reduction toward valuable compounds (e.g. fuel additives and intermediates). Hydrogenations in the presence of high pressure molecular hydrogen has been widely investigated and, in most cases, leads to the effective and selective formation of γ-valerolactone (GVL), a promising, innovative, bio-based solvent and fuel additive.[1] Nonetheless, GVL may be obtained also through the catalytic transfer hydrogenation (CTH) of LA/LE, using alcohols as reducing agents for the carbonyl group. Most of the studies published for the CTH of LA and its esters have been performed in liquid phase using batch reactors, secondary alcohols (i.e. 2-propanol) as H-donor and ZrO_2 as heterogeneous catalyst.[2] However, very long reaction time and high autogenic pressures are needed in order to work in the liquid phase at high temperature with light alcohols. Recently, we reported on the possibility to enhance the CTH of alkyl levulinates with ethanol (and bio-ethanol) in a continuous-flow, fixed bed, gas-phase reactor using a relatively high-surface-area tetragonal ZrO_2. In this way, by working at 250°C and atmospheric pressure with a contact time of just one second over the catalyst, methyl levulinate (ML) was completely converted promoting GVL formation with yield up to 70%.[3,4] Unfortunately, our catalyst undergoes to a progressive deactivation, due to the deposition of heavy carbonaceous compounds over the Lewis acid sites, finally promoting unwanted alcoholysis and transesterification reactions. Therefore new efforts have been made to strongly limit the deactivation rate and push our selectivities beyond GVL, in this way trying to assess the versatility of this gas-phase, continuous-flow approach.

Experimental/methodology. Zr-based mixed oxides have been synthesised through co-precipitation or hydrothermal synthesis depending on the case. Catalytic tests have been performed in a fixed-bed, tubular glass reactor and the desired mixture of ML and ethanol has been continuously fed in a heated line together with nitrogen in order to obtain an instant vaporisation and mixing before the reaction section.

Results and discussion. We proved that the deactivation rate is strongly affected by the surface acid-base properties of the catalyst (sites strenght and density) and these can be effectively modulated either by changing zirconia crystalline phase, the monoclinic one being the most affected by deactivation, promptly promoting parasite oligomerization reactions of the intermediate angelica lactones and acetaldehyde, or by promoting the synthesis of Zr-based mixed oxides (e.g. by the inclusion of Ti or Si). The latter strategy allows us not only to improve catalyst stability but also enhance consecutive reactions on GVL toward the efficient production of C5 esters (e.g. ethyl pentenoates and ethyl pentanoate) with a minor contribution of C7 due to the inclusion of ethanol in the final molecule via aldol condensation.

Acknowledgments
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BTEX from Lignin using a Novel Molybdenum Carbo-nitride@Titanium Nitride Catalyst

Matthew Y. Lui[1], Alexander K.L. Yuen[2], Stuart Bartlett[3], Stuart Anthony F. Masters[2], Thomas Maschmeyer[2,*]

[1] *Department of Chemistry, Hong Kong Baptist University, Hong Kong*
[2] *School of Chemistry, The University of Sydney, Sydney, 2006, Australia*
[3] *Diamond Light Source, Harwell Science & Innovation Campus, Didcot, Oxfordshire OX11 0DE, UK*
[*] *thomas.maschmeyer@sydney.edu.au*

Keywords: catalysis, supercritical ethanol, BTX, lignin, EXAFS

Introduction.

This study unveils the key structural features and compositional aspects of several molybdenum hemicarbide-based catalysts using a combination of synchrotron techniques, X-ray diffraction and elemental mapping in conjunction with electron microscopy [1] as well as their catalytic performance in the conversion of lignin to BTX using supercritical ethanol and base. [2]

Experimental/methodology.

The molybdenum hemicarbides as well as a molybdenum carbo-nitride composite material were prepared by thermal decomposition of a molybdenum–melamine polymer in the presence of titanium nitride at 650 °C under a reducing atmosphere. The catalytic reactions were performed in supercritical ethanol at between 280 and 330 °C and the samples anaylsed using a variety of spectrocopic and chromatographic techniques.

Results and discussion.

The composite was shown to be more effective than either Mo_2C or Mo_2N for the hydrodeoxygenation of lignin to single-ring arenes in supercritical ethanol. Extended X-ray absorption fine structure experiments at 330 °C, under a stream of ethanol vapor to approximate in situ conditions, elucidate the importance of the interaction of the titanium nitride support with the molybdenum carbo-nitride phase. The titanium nitride and molybdenum carbide phases are intimately mixed and, surprisingly, the result of the EXAFS analysis is consistent with the incorporation of terminal Mo≡N motifs.

Supported molybdenum hemicarbide catalysts were prepared and employed for the depolymerization and deoxygenation of waste lignins to aromatics in supercritical ethanol. Titanium nitride appears be a particularly beneficial support material. Depolymerization at 330 °C led to a higher yield and selectivity for arenes than at 280 °C. Base is essential for efficient substrate conversion: the basic constituents inherent in waste lignins are suitable, as is added sodium hydroxide. Without base, depolymerization is poor, the yield of aromatics is very low, and substrate defunctionalisation does not occur. A significant proportion of aromatic products is formed from supercritical ethanol itself, including benzene, which is likely to be present in all catalytic runs due to ethanol aromatization. Hence the total arene content produced is actually higher than has been widely reported. Catalytic cracking of ethanol leads to C1-units, which add to reaction intermediates to give aromatics containing odd numbers of carbons (e.g. toluene).

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A new method to control dispersion of transition metal catalysts and its application for biomass valorisation

Michael Stockenhuber*[1], Penghui Yan[2], Eric Kennedy[1], Luke Harvey[1] and Matthew Drewery[1]
[1]*University of Newcastle, Newcastle Australia* [2]*University of Queensland, Brisbane, Australia*
*michael.stockenhuber@newcastle.edu.au

Keywords: Hydrodeoxygenation, dispersion, catalyst synthesis, biocrude, Jet-A1, BTX Biomass, zeolites, redox, acidity

Introduction

For small or negative carbon footprint liquid fuels and commodity chemicals from unconventional renewable and sustainable sources new technological approaches have to be developed. In particular moving away from low oxygen content fossil hydrocarbon feedstocks requires the development of new chemical processes and possibly decentralisation of fuel production. Some energy carriers like air transportation fuels and also commodity chemicals will be important in the foreseeable future. To decarbonise these products, renewable sources can be used. In this lecture, new developments in controlling selectivity and productivity of hydrodeoxygenation and (de)aromatisation with an emphasis on valorisation of biomass to fuels and chemicals is presented. In particular, the emphasis will be on a new method to increase dispersion in transition metal catalysts and its application in biomass hydrotreatment.

Results and discussion

We have developed heterogeneously catalysed reaction technology that is highly selective to desired products The detailed properties of catalysts play an important role in oxidation and reduction as well as cracking reactions over heterogeneous catalysts. In particular redox activity plays an important role in tuning the selectivity of the catalyst towards hydrogenation [2] [3-5] and acidity [6] plays an important role in ring opening, cracking and deoxygenation of the biocrude feedstock originating form lignocellulosic sources. High catalyst dispersion, i.e., available metal surface atoms influence selectivity significantly [4] and reduces catalyst cost. In this paper we report a novel method that is applicable to a number of transition metals to increase metal dispersion. Herein, we present a novel facile method (vacuum-heating) which employs a specific thermal vacuum processing protocol of catalysts to promote the decomposition of metal precursors. The removal of coordinated H_2O by controlling the atmosphere and heating cycles restricts the formation of intermediates (metal-bound OH species), resulting in catalysts with a uniform, metal nanocluster distribution. *In situ* FTIR, temperature-programmed decomposition and XAS measurements were used to characterise the structure of and chemistry of the intermediate species[1]. We demonstrate how the development of a fundamental understanding of acidic and redox properties of catalysts leads to the improvement of heterogeneous catalytic processes for industrial applications.

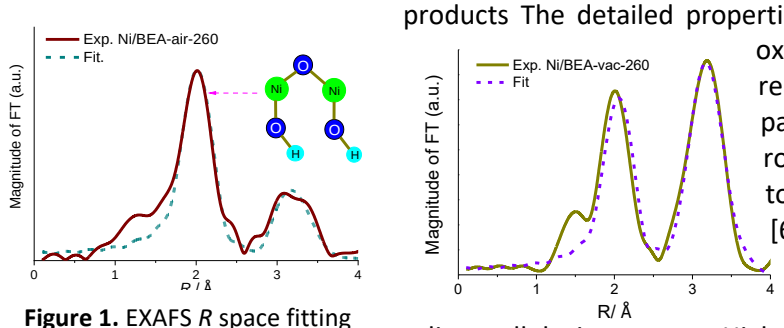

Figure 1. EXAFS *R* space fitting curves of Ni/BEA-air-260 and Ni/BEA-vac-260 from [1]

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Extending catalyst lifetime of Sn-Beta through a tandem reduction/oxidation

J. S. M. Espin[1]*, A. Katerinopoulou[1], S. Tolborg[1], E. Taarning[1]
[1]*Topsoe A/S, Haldor Topsøe Allé 1, Kgs. Lyngby, Denmark (*jsme@topsoe.com)*

Keywords: Lewis acidic catalysts, Sn-Beta, biomass conversion, regeneration.

Introduction. The lewis acidic catalyst Sn-Beta has been found useful in the conversion of sugars to functional chemicals with potential for industrial application.[1] However, some challenges still slow down the industrial implementation of this tin-based catalyst. The high reactivity of bio-based oxygenated reactants limits the operational conditions to low temperature and liquid phase employing mostly polar solvents.[2] Zeolites are known to suffer under these harsh conditions leading not only to reversible deactivation from carbonaceous build-up but also leads to a re- and destructuring and thus loss of activity during use.[3, 4] In this work, we present insight into the operation of Sn-Beta during sugar conversion and implementing a way of recovering lost catalyst activity on spent by forcing the redistribution of tin into active position after use.[5]

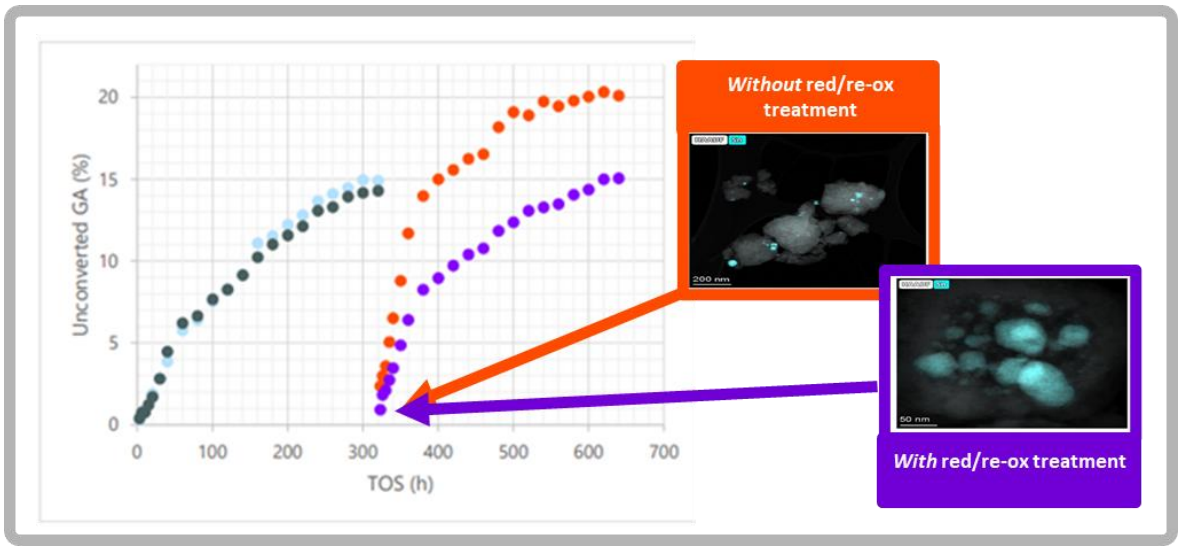

Figure 1. Unconverted glycolaldehyde (GA) as a function of TOS in hours showing the difference between employing a simple oxidative regeneration (orange) or a tandem reduction/oxidation treatment in-between cycles.

Experimental/methodology. Sn-Beta catalysts were prepared using the methodology described in [1]. The catalyst were deactivated in a GA-containing feed (PFR, 160-180°C) and the spent catalysts were treated in different gas compositions at varying temperature and subsequently tested and characterized by spectroscopic and microscopic methods to compare recovery of activity and material differences.

Results and discussion. By implementing a tandem reduction-reoxidation treatment in the regeneration protocol of Sn-Beta during use in-between cycles, catalytic activity can be recovered as shown by a cycle-to-cycle comparison in Figure 1 to yield similar deactivation profiles in the 1st and 2nd use of the same catalyst. The recovered activity can be related to changes to the material after treatment as observed by microscopy, where lost and trapped tin – observed as tin oxide agglomerates – disappear and redistribute following the tandem treatment with spectroscopic data indicating what is likely the re-creation of active tin sites otherwise lost. This recovery and reforming of tin sites will significantly extending the catalyst lifetime.

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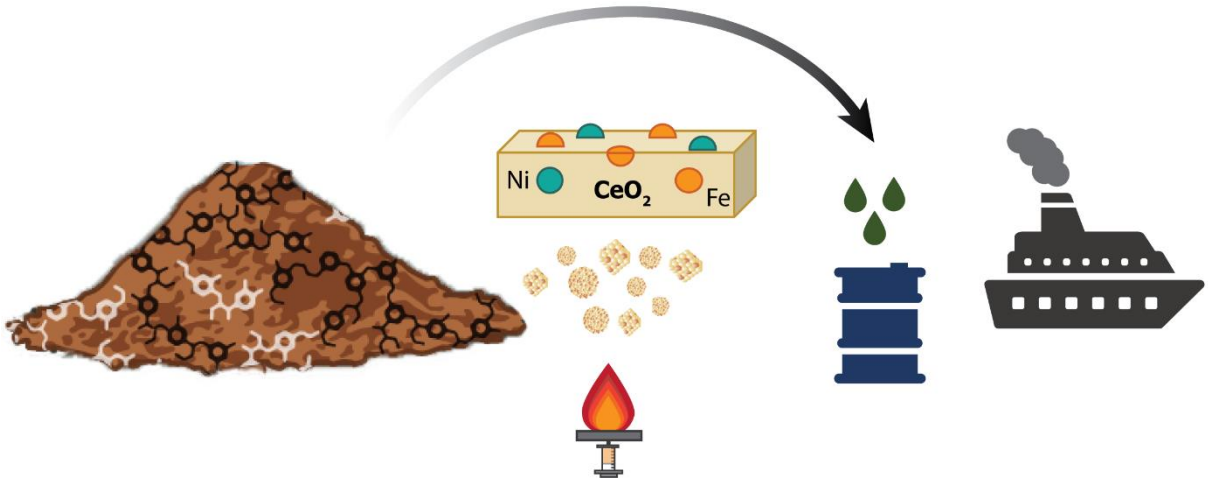
Ceria-supported Bimetallics as Catalysts for Upgrading of Lignin to Marine Fuel

Alexandra Radu[1], Savvas Kavoukis[1], Panos D. Kouris[1], Michael D. Boot[1], and Emiel J.M. Hensen[1]
[1]Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

Keywords: hydrodeoxygenation, bimetallic catalysis, biomass, bio-oil

Anthropogenic greenhouse gas emissions are expected to more than double in 2050 for the maritime sector in a business-as-usual scenario.[1] While petroleum-derived fuels are dominant, the potential of lignin as a source of renewable maritime fuels with a considerably lower environmental impact remains relatively untapped.[2] Moreover, delivering lignin derived drop-in fuels would significantly contribute to the economics of future biorefineries. Upgrading lignin by hydrodeoxygenation (HDO) has been proven difficult due to the recalcitrance of this aromatic biopolymer against depolymerization and the harsh conditions required for hydrotreatment. The product composition in terms of monomers, dimers and oligomers determines to a large extent the viscosity, which is a key specification for acceptance as marine fuel. To decrease the polarity mismatch with conventional marine fuel, oxygen needs to be removed. A novel approach is transition metal doping of reducible supports, which leads to oxygen vacancies.[3] In this work, a mild HDO route is presented involving synergetic effects between Fe and Ni on reducible supports such as ceria. A comparison is made to conventional supports. GPC shows that bimetallic transition metal catalyst lowers the molecular weight of various lignin feedstocks by two orders of magnitude in comparison to a Pd/C reference. The deoxygenation performance is determined via model compound studies, showing a 96% selectivity towards hydrogenated products. Structure-activity relations of the developed systems are investigated by XRD, XPS, STEM EDX, H2-TPR, N2-physisorption and Mössbauer spectroscopy. Products were analyzed with GC-FID/MS and 2D-HSQC NMR.



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Waste vegetable oil as a source of Green fuels

P. Reñones, D. García-Perez, J. M. Campos-Martin*

Instituto de Catálisis y Petroleoquímica (ICP), CSIC, Marie Curie, 2, 28049 Madrid (Spain)

**Corresponding author*: jm.campos@csic.es

Keywords: HVO, hydroisomerization, green fuels.

Introduction

Nowadays energy generation plays a critical role in our society, developing new processes to obtain clean and renewable energy, to decrease the CO_2 emissions mainly caused by the use of fossil fuels. Green fuels appear as good candidates for this goal, they can be obtained from biomass residues and drop-in in the current infrastructure, transport, and storage [1].

This research's purpose is related to the hydrotreating of vegetal oil (HVO)/hydroisomerization (HISO) process for obtaining green diesel and kerosene. The HVO unit yields a mixture of lineal hydrocarbons that cannot be employed directly as fuel, because several properties are not adequate, especially cold behavior. In the second step, HISO, the mixture of a part of lineal hydrocarbons is converted into branched hydrocarbons, this new mixture has exceptional properties as fuel. The catalysts and the operational conditions in each stage were picked with the aim of maximizing the conversion, the selectivity to desired products and the yield of both reactions, having into account the scalability of the process.

Experimental/methodology.

Nickel-based catalysts on alumina-supported tungsten oxides (15 wt. % W) with different loadings of nickel (0.5-10 wt. % Ni) were synthesized to study the role of Ni loading on the hydroisomerization of n-dodecane. The catalysts were prepared by wetness impregnation method on the supports to introduce W and Ni.

The hydroisomerization performance of each catalyst was tested in a trickled-bed mode reactor, worked in parallel flow, at 300ºC and high pressure (20 bar) [2].

Results and discussion.

The nickel particles were deposited over Al_2O_3 support, which has been modified with WO_x to increase its acidity. The activity results reveal an optimum balance between metal and medium-strength acid centers, which favors a fast desorption rate of the intermediates involved in the isomerization reactions, being the catalyst that contains a 6 wt. % Ni the best candidate (Figure 1). The employ of large nickel particles (> 6 wt. % Ni) favors the cracking reactions instead of isomerization reactions, due to a less Ni dispersion and higher acidity, corroborated by XRD, XPS, and NH_3-TPD analysis, decreasing the yield of the reaction.

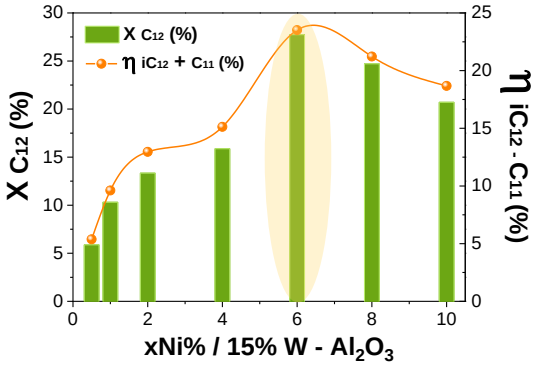

Figure 1. Conversion and yield obtained with xNi/15%W-Al_2O_3 catalysts for the hydroisomerization of n-dodecane.

The results confirmed the use of nickel-based catalysts for n-alkane hydroisomerization is a possible alternative for reducing the cost of the catalyst and the availability of the metal, compared with platinum-based catalysts usually employed.

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Emulsion templated unsupported micropsherical catalysts for slurry phase hydrotreatment of lignocellulosic bio-oils

A. Reznichenko *, T. Viertiö, A. Tuisku, E. Högnabba, J. Kihlman, J. Lehtonen

VTT Technical Research Center of Finland, Espoo, Finland
**alexander.reznichenko@vtt.fi*

Keywords: slurry hydrotreatment, bio oils, hydrodeoxygenation, emulsion, microsphere synthesis

Introduction. Thermochemical liquefaction of residual lignocellulosic biomass results in sustainable bio-oils which can in turn be further upgraded to fossil-free chemicals and fuels via hydrotreatment approach [1]. Slurry hydrotreatment allows for a robust upgrading of lignocellulosic bio-oils via continuous addition, circulation and removal of catalyst and unreacted feed [2]. In this light, development of low cost, high activity hydrotreatment catalysts compatible with slurry process and catalyst recovery operation is an important challenge to be solved for successful commercialization of pyrolysis oil upgrading to transportation fuels and biochemicals.

Experimental. Unsupported Co-promoted molybdenum sulfide based catalysts for slurry hydrotreatment of bio oils were prepared via emulsion templated synthesis. Broad range of synthesis conditions including type and amount of surfactant, nature of dispersed and continuous phases as well as emulsion solidification conditions were explored. Liquid-liquid emulsion precursors were characterized with laser scattering technique to determine stability and droplet size distribution. Solid catalysts were characterised with XRD, physisorption, XPS, ICP-AES and SEM-EDS. Both emulsions and ex situ solidified catalysts were tested in the hydrotreatment of the model compound isoeugenol in a batch reactor at 300 °C and 30 bar. Furthermore, the catalysts were tested in semi-batch hydrotreatment of fast pyrolysis bio-oil to compare the performance and evaluate the conclusions drawn from model compound experiments.
Catalyst performance was benchmarked against traditional supported sulfided hydrotreatment catalysts.

Results and discussion. Emulsion concentration, agitation regime, nature and amount of surfactant were all found to affect droplet size distribution of the stable water-in-oil emulsions containing catalyst precursors components in dispersed phase droplets. Droplet size range can be effectively adjusted in a broad range of 1-30 microns, producing dispersions with narrow size distributions and low content of fines and agglomerates. Such emulsions were found to be suitable for a direct application as catalysts in model compound and bio oil hydrotreatment. Ex situ solidification of emulsions was used to study the effect of solidification conditions on the morphology, composition and catalytic performance of the microspherical catalyst particles. More details on the catalyst preparation, characterization and catalyst performance tests will be given in the final presentation.

This work was supported by Business Finland and several Finnish companies within Catalytic Slurry Hydrotreatment (CaSH) research project, grant 43385/31/2020

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Effect of the catalyst support on the physico-chemical properties of low-cost FeNi catalysts for production of renewable fuels by dihydroeugenol hydrodeoxygenation

Zuzana Vajglová[1*], Päivi Mäki-Arvela[1], Olha Yevdokimova[1], Irina Simakova[1,2], Kari Eränen[1], Teija Tirri[1], Johan Lindén[1], Dmitry Doronkin[3], Dmitry Yu. Murzin[1]

[1]*Åbo Akademi University, Turku/Åbo, Finland*
[2]*Boreskov Institute of Catalysis, Novosibirsk, Russia*
[3]*Karlsruhe Institute of Technology, Karlsruhe, Germany*
[*]*zuzana.vajglova@abo.fi*

Keywords: FeNi catalysts, hydrodeoxygenation, lignin derived, catalytic support, renewable fuels

Introduction. The current interest in lignocellulosic biomass as a source of renewable liquid fuels and chemicals is due to depletion of fossil feedstock and environmental problems associated with fossil fuels. Hydrodeoxygenation is one of the promising methods for production of fuel components by upgrading of crude oil from fast pyrolysis .

Experimental/methodology. In this work, eight low-cost bifunctional metal-acid catalysts were investigated in hydrogenation of the lignin-derived model compound dihydroeugenol in a continuous mode. As a support, materials with different porosity and acidity were selected, namely: SiO_2, γ-Al_2O_3, and a range of zeolites H-Y-5.1, USY-30, H-ZSM-5, H-Beta-300, H-Beta-38, H-MCM-48. The incipient wetness impregnation method with two impregnation steps and nominal loading 5 wt% for each metal was used to synthesised FeNi containing catalysts. Iron and then nickel were subsequently introduced using aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$, respectively.

Fresh and spent 5-5 wt% FeNi catalysts were characterized by a range of physico-chemical method such as SEM-EDX, TEM, ICP-OES, FTIR with pyridine, TPR, TGA, N_2-physisorption, Mössbauer spectroscopy, X-ray absorption in terms of XANES and EXAFS, and soluble coke extraction with CH_2Cl_2 analyzed by GC-MS.

Results and discussion. The results clearly demonstrated that the catalyst support has significant effect on the physico-chemical properties as well as on Fe-Ni interactions directly influencing catalytic results in dihydroeugenol hydrodeoxygenation in a continuous mode. Rapid deactivation due to coke formation was obtained for all catalysts except FeNi/H-Y-5.1. Overall, the most active and selective towards desired oxygen-free compounds was FeNi/γ-Al_2O_3. More details on the catalyst preparation, characterization and catalytic tests will be given in the final presentation.

Acknowledgments

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Metal oxides-supported Ru- as catalysts for the hydrodeoxygenation of lignin model compounds

Zoel Hormigón Ausejo[1], Raquel Peláez[1], Gonzalo Prieto[1], Marcelo E. Domine[1*]
[1]*Instituto de Tecnología Química, Universitat Politècnica de València, Consejo Superior de Investigaciones Científicas, Avda. Los Naranjos S/N, 46022, Valencia, Spain*
[*]*mdomine@itq.upv.es*

Keywords: Lignin, HDO process, lignin models, supported Ru-catalysts, metal oxides.

Introduction. Lignocellulosic biomass, mainly composed of cellulose, hemicellulose and lignin (15-25 wt%), is the biggest renewable source for the production of biofuels and biomaterials; lignin being the major source of renewable aromatic compounds. Its highly complex amorphous structure is formally derived of the co-polymerization of sinapyl, coniferyl and *p*-coumaryl alcohols. However, it is possible to find a series of specific linkages which are repeated more or less frequently in its structure; among those, the more predominant is β-O-4´.[1] For lignin-derived biofuel production, hydrodeoxygenation (HDO) process is required to produce hydrocarbons through oxygen removal, as well as to cleave C-C/C-O bonds present in lignin through hydrogenolysis reactions. Conversion of well-defined and chemically pure lignin model compounds was used as reference to study the role of different supported Ru catalysts, a metal known for its notable activity in HDO reactions,[2] for the cleavage of the most representative chemical linkages in lignin oligomers. Based on these results, the most appropriate catalysts for HDO of real lignin feeds can be designed. Different lignin model compounds have been considered in this study, including: 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol as representative model for β-O-4´ lignin linkages, and 2,3-dihydrobenzofuran as representative model for β-5´ linkages, respectively.

Experimental/methodology. A set of Ru catalysts supported on different metal and lanthanide oxides (γ-Al_2O_3, TiO_2, ZrO_2, CeO_2) and mixed oxides thereof (TiO_2·Al_2O_3, ZrO_2·Al_2O_3, TiO_2·ZrO_2, CeO_2·ZrO_2; prepared by co-precipitation method) were developed. Catalysts with a theoretical loading of ≈2wt% of Ru were synthesized by deposition-precipitation method and characterized by ICP-OES, XRF, XRD, N_2 adsorption isotherms, SEM and TEM, NH_3-TPD, and TPR, among other. The catalysts were activated under H_2 flow at 250 ºC for 4 h prior to their use in reaction. A 12 mL stainless steel autoclave reactor with a PEEK-reinforced with graphite wire vessel was used for catalyst evaluation in the conversion of lignin models via hydrogenation/HDO. Typically, the reactor was charged with a suspension of the catalyst (20wt% respect to lignin model) and lignin model in 2 mL of EtOH as solvent. The reactor was hermetically closed and pressurized with 40 bar of H_2. Then, the reaction mixture was heated to 240 ºC at 1000 rpm during 5 hours. Kinetics of reaction were followed by GC-FID (Agilent 7890A instrument equipped with a 30 m HP-5 capillary column), while product identification was made by GC-MS.

Results and discussion. From the different studied Ru-based catalysts, which were benchmarked against a commercial Ru/C, Ru/γ-Al_2O_3 and Ru/Ti-Al-O showed superior catalytic activity (i.e. TON) for both lignin models as well as superior HDO activity in view of the product distribution achieved. This developed Ru/γ-Al_2O_3 catalyst will be tested on a real lignin feed, a sugar-containing methanol-based crude lignin oil (CLO) derived from the processing of raw lignin in the IDEALFUEL Horizon Europe project, and compared to the commercial Ru/C, under HDO operational conditions previosuly established for benchmark catalysts.

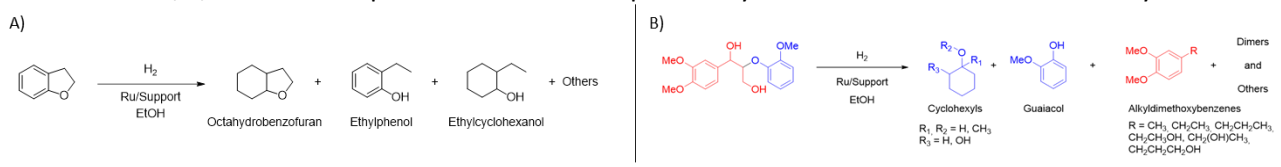

Figure 1. HDO reactions of Ru-supported catalysts studied in this work: A) of β-5' lignin model 2,3-dihydrobenzofuran and B) of β-O-4' lignin model 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol.

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Influence of Sulfation on Activity & Stability of Metal oxide Catalysts for Vapor-phase Ketonisation of Volatile Fatty Acids

G. Deshmukh[1], M. Delarmelina[2], A. Goguet[1], R. Catlow[2], and H. Manyar[1,*]

[1] *School of Chem. and Chem. Eng., Queen's University Belfast, Stranmillis Road, Belfast BT9 5AG, UK,*
[2] *School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK.*
**h.manyar@qub.ac.uk*

Introduction. The depletion of fossil fuels coupled with increasing demand for renewable carbon-neutral energy is amongst the top global challenges, and development of alternative biofuels is one of the potential solutions [1]. In this context, aqueous streams also called process waters, obtained after the biomass treatments (hydrothermal liquefaction, pyrolysis, and fermentation) are important feedstock. Aqueous streams contain up to 10% w/w carboxylic acids (chain length C_1 to C_6), which are generally referred as the volatile fatty acids (VFAs). VFAs can be upgraded to produce long chain alkanes (C_8-C_{14}) through a series of catalytic processes. The current VFA upgrading process involves ketonisation of VFAs to produce C_5-C_{11} range ketones, followed by aldol condensation of ketones to elongate the chain length. A final hydrogenation produces fuel range alkanes. In ketonisation, two molecules of carboxylic acids are condensed to form long chain ketone with the loss of one molecule of CO_2 and H_2O each (**Figure 1a**). Ketonisation of VFAs has been widely studied, but the reaction mechanism and the role of active sites such as surface acid-base pairs is not clearly understood. In this study, by combining experimental and Density functional theory (DFT) studies, we have established the reaction mechanism and the role of sulfated species on the surface of metal oxides in enhancing the catalyst activity, minimising the byproduct formation, and increasing the catalyst stability and longevity [2]. Herein, we show that upon sulfation, Brønsted and Lewis acid strength increased significantly, whereas Lewis basicity decreased. Such changes in the interplay between acid−base sites resulted in an improvement of the selectivity toward the ketonisation process, by suppressing the side reaction of acetone self-condensation. We report a detailed DFT investigation of the putative surface species on sulfated zirconia, including the possible formation of dimeric pyrosulfate ($S_2O_7^{2-}$) species. Our results show that the formation of such a dimeric system is an endothermic process, with energy barriers ranging between 60 and 70 kcal mol^{-1}, and which is likely to occur only at high SO_4^{2-} coverages (4 S/nm^2), high temperatures, and dehydrating conditions. Conversely, the formation of monomeric species is expected at lower SO_4^{2-} coverages, mild temperatures, and in the presence of water, which are the usual conditions experienced during the chemical upgrading of biofuels.

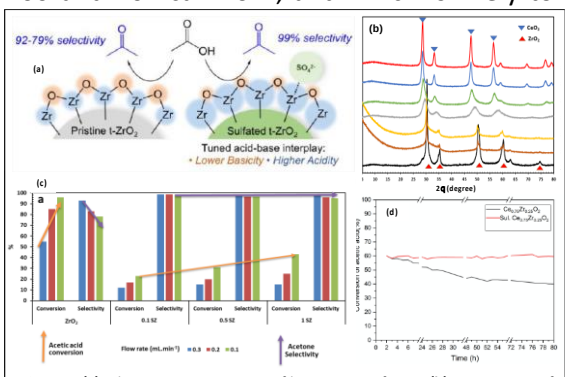

Figure 1. (a) Schematic representation of ketonisation of VFAs, **(b)** XRD patterns of different sulfated $Ce_xZr_{1-x}O_2$ catalysts, **(c)** The effect of space velocity on % conversion of acetic acid and % selectivity to acetone for pristine and sulfated ZrO_2, and **(d)** Time on stream for catalyst activity and stability.

Experimental/methodology. A series of sulfated and as synthesized $Ce_xZr_{1-x}O_2$ catalysts with varying Ce/Zr mole ratios were prepared using co-precipitation method. The ketonisation was performed in custom designed packed-bed reactor. Periodically, reaction samples were analysed using gas chromatography.

Results and discussion. The efficacy of all pristine and corresponding sulfated $Ce_xZr_{1-x}O_2$ catalysts showed that the sulfation improved the selectivity to acetone by prohibiting subsequent self-condensation of acetone. Decreasing the feed flow rate, over as synthesized $Ce_xZr_{1-x}O_2$ catalysts, enhanced the acetic acid conversions, but lowered the acetone selectivity. All sulfated $Ce_xZr_{1-x}O_2$ catalysts, showed high selectivities to acetone (95-98%). The XRD patterns of all catalysts calcined at 500 °C, reflected ZrO_2 in tetragonal phase and ceria in cubic phase (**Figure 1b**). Both sulfated and pristine $Ce_{0.75}Zr_{0.25}O_2$ catalysts showed better activity and selectivity to acetone compared to the corresponding parent metal oxides of CeO_2 and ZrO_2 (**Figure 1c**). Sulfation of the catalysts also helped to enhance the catalyst stability (**Figure 1d**). The scope of the ketonisation was successfully extended to a range of C_4-C_6 VFAs in individual and mixture of feedstocks.

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Glycerol derivatives as bio-based C_1 building blocks for N-formylation of amines to formamides with O_2 as the oxidant

Xingchao Dai[1*], Angelika Brückner[1], Feng Shi[2], Jabor Rabeah[1]

[1]*Leibniz-Institut für Katalyse e.V., Albert-Einstein-Str. 29a, 18059 Rostock (Germany)*
[2]*State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, No.18, Tianshui Middle Road, Lanzhou, 730000 (China)*
[*]*Xingchao.Dai@catalysis.de*

Introduction

The rising production of biodiesel creates a surplus of glycerol which must be valorized to turn waste into treasure. One way is selective oxidation of glycerol to 1,3-dihydroxyacetone (DHA), glycolic acid or glyceraldehyde being platform molecules for further syntheses.[1] Recently, we have demonstrated that DHA can be used as a C_1 carbonyl source instead of highly toxic CO to convert amines to formamides with H_2O_2 as oxidant.[2-4] Unfortunately, an excess of H_2O_2 was needed, due to its low utilization efficiency, partial decomposition and detrimental byproduct formation. To make these reactions more sustainable, H_2O_2 should be replaced by gaseous oxygen as a clean and cheap oxidant. In this work, we show for the first time that all carbon atoms in DHA can be utilized to convert amines to the respective formamides in the presence of molecular oxygen and a ligand-modified Cu/C_3N_4 catalyst.

Experimental

Different Cu/C_3N_4 catalysts (Figure 1) were prepared using copper nitrate and melamine as the C_3N_4 precursor by one-pot pyrolysis in the absence and presence of amino ligands such as 1,10-phenanthroline (phen) and 2,2-bipyridine (bpy). The prepared catalysts were comprehensively chracterized by different analytic and spectroscopic techniques. N-formylation of amines with DHA was performed at 150 °C with 0.5 MPa O_2 in an autoclave.

Results and discussion

Activity test results showed the highest catalytic performance for $Cu(phen)_2/C_3N_4$ in N-formylation of aniline with 90% yield of the desired formanilide (Figure 1a). With this catalyst, a range of amine substrates including aromatic, aliphatic, benzylic, primary and secondary amines can be converted into valuable formamides in good yields. Combined ex-/in-situ characterization techniques revealed that the active catalyst $Cu(phen)_2/C_3N_4$ contained a higher amount of surface Cu species and exhibited a faster Cu^I/Cu^{II} redox cycle, which may be the reason for the better catalytic activity (Figure 1b-c). Investigations of the reaction mechanism by in-situ EPR and control experiments revealed that singlet oxygen is formed by activation of O_2 on the catalyst, which may be the real oxidant (Figure 1d) and that HCOOH is the possible C_1 reaction intermediate in the formation of formamide products.

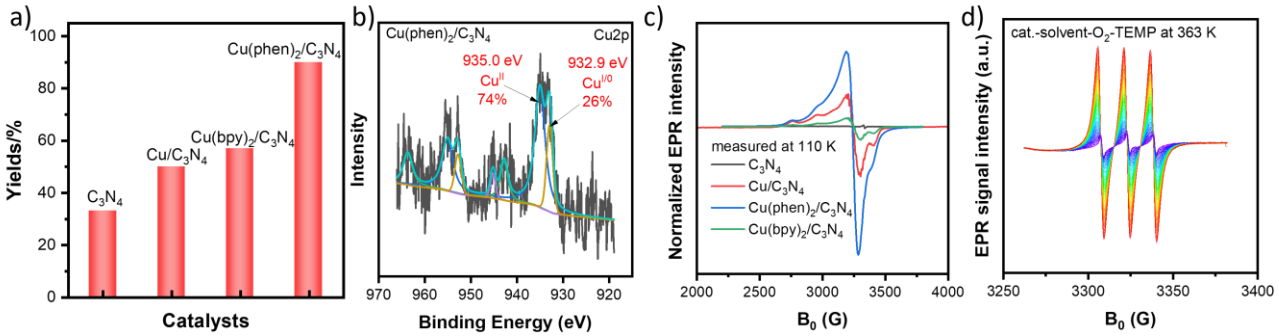

Figure 1. a) activity test and characterizations b) XPS, c) EPR and d) in situ EPR experiments.

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Catalytic conversion of biobased ketones to renewable aromatics: Influence of solid acid catalysts and reaction engineering

Phillip Reif[1], M. Rose[1*]
[1]*Chemical Technology II, Technical University of Darmstadt, Darmstadt, Germany*
[*] *marcus.rose@tu-darmstadt.de*

Introduction. Aromatics such as benzene, toluene and xylene (BTX) are important precursors for versatile industrial applications.[1] Annually more than 103 Mio. t (2012) are produced globally mainly via catalytic reforming of naphtha.[2] But limitation of fossil resources demands for sustainable routes from renewable resources such as biomass. Current approaches for bio-based aromatics focus on biomass-derived furan derivatives as raw material and pyrolysis of lignocellulosic biomass. However, these processes are based on multiple reaction steps which often lack selectivity and require complex separation. Herein, we present a one-step, solvent-free direct production of 1,3,5-substituted C6-aromatics by cyclotrimerization of biomass-derived alkyl methyl ketones which are accessible from chemocatalytic or biotechnological biorefinery processes,[3] e.g., acetone from ABE-fermentation. We proof the potential of this route using stable solid acid catalysts under batch and continuous processing conditions.[4-6]

Experimental. Acetone as well as higher alkyl ketones such as 2-butanone and 2-pentanone were used as model substrates, the consecutive aromatization via the dimer mesityl oxide to mesitylene and its derivatives was studied in liquid phase batch as well as flow conditions. Catalysts, reaction temperature and time were screened for maximum yield and selectivity to aromatics. Screening of solid acid catalysts (5 wt%) was performed in stirred batch autoclaves with acetone (10 g) at 130-190 °C (3-15 h). Time course of the reaction was studied in a batch reactor (2.5 wt% cat., 150 mL ketone) with a sampling line. Filtered product solutions were analyzed by GC and GC/MS with 1,4-dioxane (30 wt%) as internal standard and phase solubilizer. Catalyst stability was assessed in a fixed-bed reactor equipped with an online-GC at 130-230 °C at 40 bar and a WHSV of 8 h^{-1} using 3 g of shaped catalyst particles.

Results and discussion. From a screening of 30 solid acid catalysts, ion exchange resin Purolite CT275DR, beta-zeolite H-BEA 35 and amorphous silica-alumina Siralox 70/170 were selected based on their mesitylene yield. The overall highest aromatics yield (15.8 % at 160 °C, 6 h) was found for Purolite, that turned out to be less selective at higher temperatures. Time-resolved experiments identified two consecutive phases with a high initial activity in the first 20-30 min and a subsequent activity drop. This is marked by a maximum in the dimer yield, whereas acetone conversion and consecutive product yields constantly increase over time. It was found that the aromatization activity generally increases with acid site density but is not dependent on acid strength. Reactions in continuous liquid flow revealed that Purolite was not thermally stable at elevated temperatures (150 °C) and that the majority of tested zeolites deactivated once aromatization activity was observed. In contrast, the amorphous silica-alumina Siralox 70/170 was highly stable for more than 35 h-on-stream at 230 °C and showed constant acetone conversion and mesitylene production. No significant catalyst deactivation was observed which is supported by TGA. In conclusion, amorphous silica-alumina was found to be stable and efficient for the one-step conversion of biomass-derived ketones. The high stability of the catalyst under liquid phase conditions is essential for the establishment of a new environmentally benign process for alkyl methyl ketone aromatization.

Acknowledgments
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Vapour phase upgrading of acetic acid over noble metal promoted metal oxides at hydropyrolysis conditions: reaction mechanisms and pathways

P.Tingelstad[1*], D. Chen[1]

[1]Norwegian University of Science and Technology, Trondheim, Norway.

Keywords: biomass pyrolysis, vapor phase upgrading, fundamental catalyst study, acetic acid.

Introduction.

Acetic acid is a main product from hydropyrolysis of biomass, account for up to 10 wt% of the formed products. Vapor phase upgrading directly after the pyrolysis reactor offers an attractive pathway for converting the low molecular weight and water soluble compounds to long chain hydrocarbons and aromatics. Acetic acid is explored here both as a model compound for other oxygenates, as well as a major naturally forming product of the pyrolysis process. Converting the acetic acid to longer chain hydrocarbons and aromatics offers an attractive route for increasing the carbon yield by 6 wt%-points [1]. Herein, the vapor phase conversion of acetic acid over noble metal promoted metal oxides is studied.

Experimental/methodology.

In this study, laboratory experiments were conducted in a PID Microactivity Reference unit with continuous flow of acetic acid (3 mol%), hydrogen (20 mol%), and nitrogen (77 mol%) over promoted TiO2 catalysts. The exit gas was analyzed by GC-FID/MS for quantitative and qualitative analysis. All mass balances were over 97 %.

The catalysts were characterized by XPS, XRD, TEM, Chemisorption and BET. The lewis acidity and bacicity was determined by CO2 and NH3 calorimetry.

Results and discussion.

All products were determined by GC-FID/MS. The pathway for all formed products were determined. Acetone was always the main product formed, with acetaldehyde being the second highest. These two molecules act as the main building blocks for the rest of the formed products, and their pathways can be seen in Figure 1. Mass balance closure was always above 97 %.

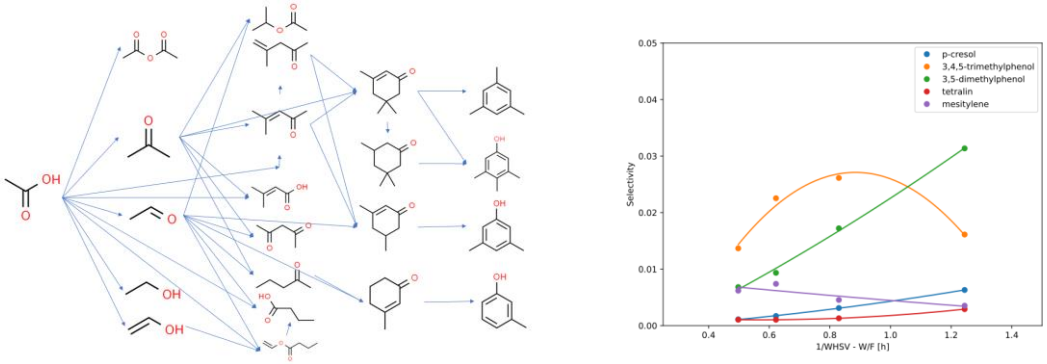

Figure 1: Reaction pathway for all formed compounds and selectivity of aromatics as function of spacetime. T = 350 °C, WHSV = 0.5-2.0 h, P = 1 atm. X/TiO2 = 0.600 g, 2.000 g SiC used as diluent. 3 mol% acetic acid, 20 mol% H2, 77 mol% N2.

A kinetic model has been developed that calculates the rate constant for each reaction as a function of catalyst only, the temperature has been set at 350 °C for all experiments. XPS has given the oxidation state of each element, and a statistical model is under construction that correlates the oxidation state and chemical bonds of each element (Ti, O, noble metal) to the reaction rate between each molecule. Selective doping of the catalyst by NH3 is also being investigated, to elucidate the active site.

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Stepwise approach for selective FFCA and FDCA production from HMF

J.J. Wiesfeld[1], R. Osuga[1], E.J.M. Hensen[2], K. Nakajima[1*]
[1]*Institute for Catalysis, Hokkaido University, Sapporo, Japan*
[2]*Laboratory of Inorganic Materials and Catalysis, Eindhoven University of Technology, the Netherlands*
[*]*nakajima@cat.hokudai.ac.jp*

Keywords: Biomass, Heterogeneous catalysis, HMF, Protection strategy

Introduction 2,5-Furandicarboxylic acid (FDCA) can potentially replace terephthalic acid, used for the production of PET polymer. Its starting material 5-hydroxymethylfurfural (HMF) is thermally unstable, leading to undesired condensation products in FDCA production using concentrated HMF solutions. The instability stems from its very reactive formyl group. Recently, our group reported the production of FDCA in high yield (>92%) from concentrated solutions (>10 wt%) of HMF protected as its acetal (HMF-A) with 1,3-propanediol (PDO).[1] PDO itself is slowly liberated during the reaction and partly oxidized, which lowers its recoverability (80%). We devised a stepwise approach (Fig. 1A) which separates the oxidation reaction from the deprotection step, while maintaining high FDCA yield.

Experimental Au/HAP catalyst was prepared via NaOH-assisted deposition precipitation.[1,2] HMF-A and FFCA-A were prepared as described in earlier works.[1] Oxidation reactions were performed in PTFE-lined batch reactors. Relevant reaction conditions are listed in the caption of Fig 1.

Results and discussion Kinetic data show that full conversion of aqueous 10 wt% HMF-A required 2 hours and produced FFCA-A in 94% yield through DFF-A as an intermediate (Fig. 1B). FDCA was formed only in minor quantities due to the high stability of PDO acetal in alkaline environment which prevented further oxidation. FFCA-A was then deprotected by acidifying the reaction mixture to pH 1, followed by a 4 hour heat treatment at 65 °C. Extraction of the aqueous solution with ethyl acetate yielded 99% of FFCA, while 94% of the PDO introduced as HMF-A remained in the water layer. FFCA in concentrations up to 20 wt% could be oxidized to FDCA (96% yield) without significant byproduct formation (Fig 1C).

Conclusions Concentrated HMF-A (10 wt%) was selectively oxidized to FFCA-A with only minor byproduct formation, owing to the acetal stability. FFCA-A was facily deprotected by lowering the pH and 94% PDO could be recovered after extraction and separation. Up to 20 wt% FFCA could be oxidized to FDCA. Overall yield was 90%.

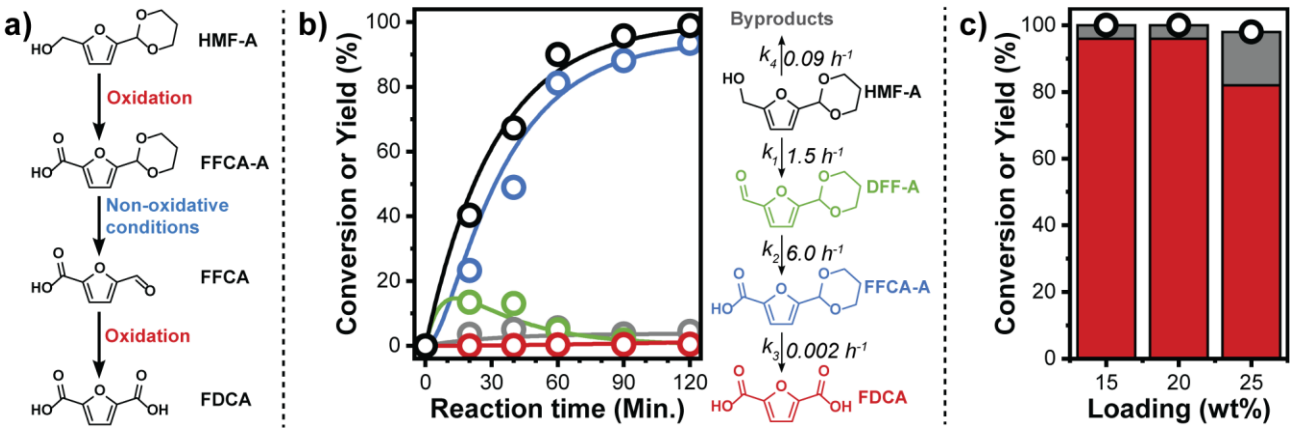

Fig 1. a) Stepwise approach scheme, b) HMF-A oxidation time course. Conditions: 100 mg HMF-A in 1 mL H_2O, 2 mol. eq. Na_2CO_3, 0.5 MPa O_2, 100 °C, c) Oxidation of FFCA to FDCA. Conditions: 150-250 mg FFCA in 850-750 µL H_2O, 1.5 mol. eq. Na_2CO_3, 0.5 MPa O_2, 140 °C, 5 h. Products are represented by molecules of the same color, black circles display conversion. Byproducts are shown in grey.

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Aqueous-phase reforming of ethylene glycol over platinum-based catalysts supported on functionalised carbon nanofibres

M. Pazos Urrea[1], F. Herold[1], S. Meilinger[1], E. Tusini[2], A. De, Giacinto[2], A. Zimina[2], D. Chen[1], M. Casapu[2], J.-D. Grunwaldt[2], M. Rønning[1]*

[1]*Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway.* [*]*Corresponding author: magnus.ronning@ntnu.no*

[2]*Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT) Engesserstraße 20, 76131 Karlsruhe, Germany*

Introduction.
Aqueous phase reforming (APR) is a process for producing H_2 from low-value mixed oxygenated compounds [1]. It allows for utilization of biomass-derived waste streams to valuable products at relatively mild reaction conditions. The stability of the catalysts are affected during APR, with metal leaching, sintering and coke deposition as the main deactivation mechanisms [2]. Carbon materials possess good hydrothermal stability compared to metal oxides, are resistant to acidic and basic media and the physical properties can be tailored, such as surface functionalisation and heteroatom doping [3].

Experimental/methodology.
Pt and Mn-based monometallic and bimetallic catalysts were synthesized by incipient wetness impregnation supported on carbon nanofibres (CNF) produced by chemical vapour deposition and treated it in nitric acid to introduce surface oxygen groups (CNF-ox) and heat-treated at 700°C to remove the oxygen groups (CNF-H). N-doping of the CNF with ethylene diamine as the nitrogen source was performed at 875°C at 10°C/min in N_2 (CNF-N). The catalysts were characterized by BET, CO chemisorption, XPS, MP-AES and STEM-EDS. In situ XAS-XRD was performed at the Pt L_{III} and Mn K edges at continuous flow APR conditions. APR of ethylene glycol was performed at 225°C and 20 bar initial pressure in batch, and 30 bar pressure in continuous reaction using as feed of 6 wt% ethylene glycol in water.

Results and discussion. The effect on the APR performance by functionalizing carbon supports with nitrogen and adding Mn to Pt-based catalysts was investigated. Bimetallic catalysts such as PtMn supported on N-doped carbon nanofibres are active and selective catalysts for aqueous phase reforming of ethylene glycol, with H_2 site time yield of 15.8 min^{-1} at 225°C and 30 bar pressure. The enhancement in catalytic activity could be attributed to metal-support interactions between PtMn and N-doped carbon nanofibers, decreasing the electron density on Pt and promoting H_2 formation. The addition of Mn to the Pt-based catalysts further decreased the electron density of Pt by metal-metal interaction and increased the catalytic activity.

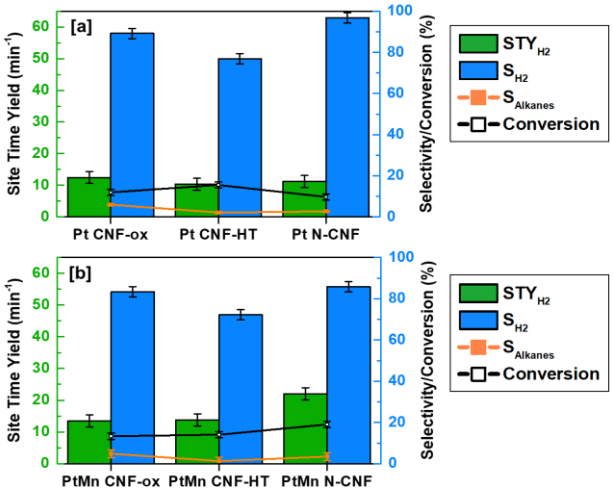

Figure 1: APR of ethylene glycol at 225°C and 20 bar initial pressure in batch. Conversion of EG, H_2 STYH_2) H_2 and alkane selectivities for the [a] monometallic Pt and [b] bimetallic PtMn catalysts

Acknowledgments
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Continuous synthesis of nylon intermediates from bio-based γ-valerolactone

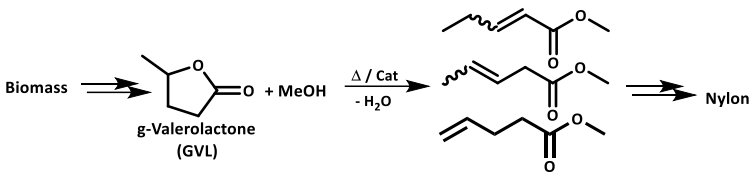
A. Marckwordt, V.N. Kalevaru*, S. Tin, J.-G. de Vries, S. Wohlrab

Leibniz Institute for Catalysis, Albert-Einstein-Str. 29a, Rostock, 18059, Germany

* narayana.kalevaru@catalysis.de

Keywords: renewable resources, biomass, γ-valerolactone, pentenoates, gas-phase reaction

Introduction. There is a growing demand for the production of nylon precursors from renewable resources, not only due to dwindling supply of fossil resources, but also because the current production processes of nylon are associated with a rather high carbon footprint. Lignocellulosic biomass is an ideal raw material for the production of building blocks, e.g. levulinic acid that can be hydrogenated to γ–valerolactone (GVL) [1]. Conversion of GVL into an isomeric mixture of methyl pentenoates (MP) via a ring-opening transesterification and dehydration reaction is one good option for the utilisation of bio-based feedstocks to produce nylon intermediates. The terminally unsaturated methyl 4-pentenoate (M4P) can be converted into a nylon-6 precursor, ε-Caprolactam, while the remaining M2P and M3P isomers can be converted to adipic acid, a nylon-6.6 precursor (Scheme 1). The aim of this study is to develop highly active and selective catalysts with a special emphasis devoted to understand the interconversion process of MP isomers due to C=C double bond isomerisation during the course of the reaction.



Scheme 1. Conversion of GVL into MPs

Experimental/methodology. Various ZrO_2/SiO_2 catalysts were prepred by impregnation[2]. The content of Zr was varied in the range from 2.5 to 30 wt%. The catalytic tests were carried out in a fixed bed tubular reactor in a gas phase continuous process in the temperature range of 255 to 335 °C. The products were collected in an ice-cooled trap and analysed by GC equipped with FID.

Results and discussion. Among all catalysts, 25 % Zr/SiO_2 exhibited the best performance. The influence of various key reaction parameters on the activity/selectivity was explored and suitable reaction conditions were optimised. The conversion of GVL and product distribution was found to be strongly dependent on the reaction temperature. The GVL conversion increased from 44 % to 85 % with rise in temperature from 255 to 315 °C and then levelled-off beyond this temperature. The sum selectivity of all the three MP isomers is varied in the range from 97 to 99 %. At low temperature (255 °C), M4P was the major product while M2P was minor product. However, with increase in temperature, the selectivity of M2P and M3P increased at the expense of M4P due to isomerisation of C=C double bond. In addition, the long-term stability of 25 % Zr/SiO_2 catalyst was examined and found that the catalyst displayed consistent performance with an excellent long-term stability for a period of >340 hours-on-stream. In order to gain deeper insights on the isomerisation of MPs, a set of control experiments were also performed by dosing individual MPs as educts under similar reaction conditions. These results indicate that M4P can be converted mainly to M3P and also partly to GVL due to ring closing. However, dosing of either M3P or M2P as a reactant did not result in the formation of either GVL or M4P. On the other hand, M3P can be easily converted to M2P isomer and vice versa. In summary, it can be stated that the key reaction parameters need to be selected carefully for better tuning of the product distribution in the desired way. Based on these results, we also proposed the most probable reaction pathway for the conversion of GVL into MPs.

Acknowledgments

We thank the Leibniz Foundation for the funding of the project: Agro and Paper Industry Waste to Bulk Chemicals, Levulinic acid and Furfural as Platform Chemicals (SAW-2016-LIKAT 1 523).

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Selectively oxidizing methane to formaldehyde over platinum nanoalloy catalysts in the presence of water

S. V. L. Mahlaba[1*], G. M. Leteba[1], A. Govender[2], E. J. Olivier[3], E. van Steen[1]

[1]*Catalysis Institute, Department of Chemical Engineering, University of Cape Town, Private Bag X3, Rondebosch 7701, South Africa*

[2] *Sasol R&T, Sasol South Africa (Pty) Ltd., Klasie Havenga Road, Sasolburg 1947, South Africa*

[3] *Centre for HRTEM, Physics Department, Nelson Mandela University, Port Elizabeth, South Africa*

[*]*eric.vansteen@uct.ac.za*

Keywords: Aerobic methane oxidation, alloys, C_1 catalysis, selective oxidation

Introduction. Methane is an abundant carbon source (from natural gas and landfill sites) that can also be obtained sustainably through the anaerobic digestion of biomass. Methane is currently used for heating, power generation or synthesis of fuels and chemicals. The latter requires the reforming of methane to syngas (CO and H_2) under demanding conditions [1]. The direct conversion of methane, via oxidation to oxygenates under relatively mild conditions presents an opportunity for the efficient utilization of this abundant carbon source for the synthesis of chemicals [2]. The direct conversion of methane to C_1-oxygenates however remains a challenge due to either low catalyst productivity [1], or the use of expensive reagents [1,3]. Furthermore, the selective oxidation of methane to methanol or formaldehyde tends to suffer from the conversion/selectivity trade-off, wherein high selectivities are only obtained at low conversions [1]. A highly productive process that utilizes oxygen as an oxidant is thus highly sought after. Herein we report on the catalytic, aerobic oxidation of methane to formaldehyde over platinum-based catalysts in the presence of water.

Experimental/methodology. The Pt, Pt_3Cu, Pt_3Ag and Pt_3Au nanoparticles (d ~ 4 nm) were synthesized using a bottom-up wet chemical synthesis approach, and subsequently supported on titania (rutile) via impregnation using chloroform as the solvent yielding 10 wt.-% metal on the support. The oxidation of methane was carried out in a packed bed reactor fitted with a quartz liner at 220°C at elevated pressure.

Results and discussion. The rate of methane consumption over the platinum-based catalysts increases with increasing ratio of water to methane in the feed and reached 300 μmol/g/hr over the Pt_3Cu catalyst, followed by Pt and Pt_3Au, with Pt_3Ag being the least performing. The selectivity towards CO, CO_2 and CH_2O were similar across all catalysts with the formaldehyde selectivity increasing with increasing conversion. The Pt_3Cu/TiO_2-rutile displaying the most promising performance for aerobic, selective oxidation of methane.

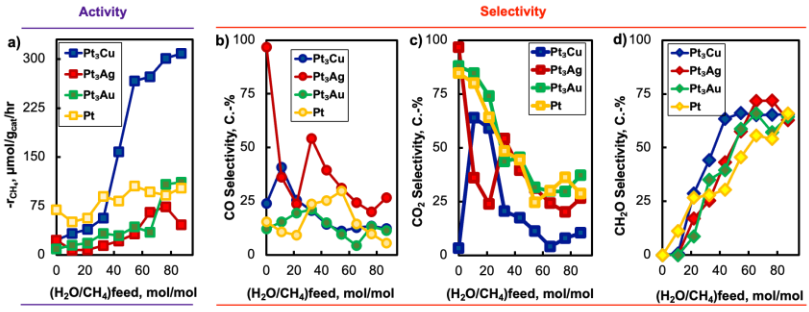

Figure 1: Rate of methane conversion (a) and product selectivity (b-d) over supported Pt-based catalysts as a function of the molar ratio of water to methane in the feed.

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Continuous transfer hydrogenolysis of THFA to 1,5-pentanediol over stable Ni-La(OH)$_3$: Towards selective synthesis of bio-based α,ω-diols

M. Al-Yusufi[1*], D. Michalik[1,2], N. Steinfeldt[1], M. Sebek[1], H. Atia[1], R. Eckelt[1], C. Kubis[1], T. Ishida[3], T. Murayama[3], A. AbdelMageed[1], A. Köckritz[1*]

[1]*Leibniz Institute for Catalysis (LIKAT), Rostock, Germany*
[2]*University of Rostock, Rostock, Germany*
[3]*Tokyo Metropolitan University, Tokyo, Japan*
[*]*mohammed.al-yusufi@catalysis.de,* [*]*angela.koeckritz@catalysis.de*

Keywords: α,ω-diols; 1,5-pentanediol; furfural; THFA; nickel; catalytic transfer hydrogenolysis, isopropanol

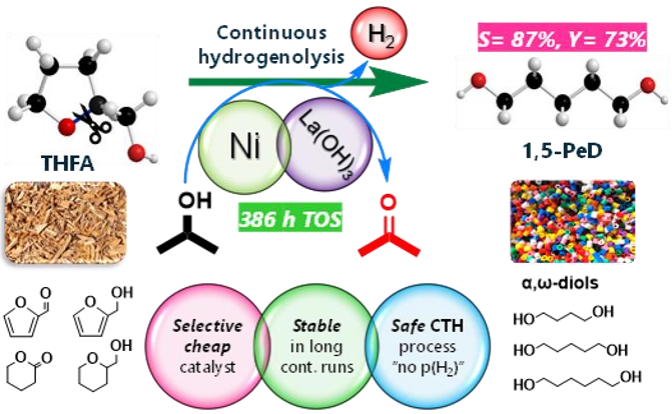
Introduction.

α,ω-Diols, such as 1,5-pentanediol (1,5-PeD), are value-added monomers produced from petrochemicals under harsh conditions and widely used for producing technical plastic, polyester and polyurethane resins [1]. Due to the increased demand for these plastic materials, it is essential to develop alternative reaction routes for their synthesis from bio-based lignocellulose feedstocks. For instance, direct hydrogenolysis of tetrahydrofurfuryl alcohol (THFA) to 1,5-PeD over modified Rh or Ir catalysts [2]. However, because of the high costs of these catalysts and their low stability in the continuous process [3], it is highly desired to replace them with stable and cheap nickel catalysts, which have more potential for industrial applications.

Experimental/methodology.

Nickel catalysts were prepared on lanthanum hydroxide (wt% Ni-La(OH)$_3$) by co-precipitation and sequential reduction at different temperatures [4]. The transfer hydrogenolysis (CTH) reaction conditions were optimized and compared in a batch reactor and a micro-reactor flow set-up. The catalyst stability and productivity were tested in long-term continuous runs. The structure-activity relationships were revealed using XRD, BET, TPX, XPS, XANES-EXAFS, STEM-EDX techniques. The reaction mechanism of C–O bond hydrogenolysis of THFA to 1,5-PeD was elucidated using ^{13}C NMR isotope labeling and *in-situ* FTIR.

Results and discussion.



Continuous transfer hydrogenolysis (CTH) of THFA to 1,5-PeD was developed using stable Ni-La(OH)$_3$ catalysts in the hydrogen-donor isopropanol for the first time. Remarkably, 40Ni-La(OH)$_3$ was selective to 1,5-PeD (87%) and demonstrated high stability in long continuous runs (up to 386 h TOS). A maximum 1,5-PeD yield of 73% with a productivity of 1.4 mmol g(cat)$^{-1}$h^{-1} was achieved. After evaluation of experimental and spectroscopic results, a direct hydride attack mechanism was proposed for the selective hydrogenolysis of the C–O bond of THFA on the interface between Ni and La(OH)$_3$ support. This joint interface was responsible for the high yield of 1,5-PeD over Ni-La(OH)$_3$ where the strong basic sites deprotonate the hydroxyl group of THFA, and metallic Ni species dehydrogenate isopropanol to acetone producing hydrogen. The elimination of the hazardous H_2 reduces the costs for a high-pressure apparatus and raises the level of safety in the workplace, which is as excellent advantages for large-scale industrial applications.

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A Comprehensive Investigation on the Co-Feeding of Furfural and Levulinic Acid for 2-Methyltetrahydrofuran Production using Alumina-Supported Bimetallic Catalysts

R.Q. Raguindin, Y.B. Kim, J.G. Seo*

Department of Chemical Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 04763, Republic of Korea

**Corresponding Author's E-mail address: jgseo@hanyang.ac.kr*

Keywords: Furfural, Levulinic Acid, 2-Methyltetrahydrofuran, Hydrogenation, Heterogeneous Catalysts

Introduction. The catalytic conversion of furfural (FUR) and levulinic acid (LA) expands the broad spectrum of chemicals that can be derived from lignocellulosic biomass. 2-methyltetrahydrofuran (MTHF), a widely used solvent in oil extraction and organic reactions and a gasoline additive, can be produced from both FUR and LA [1]. Several studies have reported the production of MTHF from separate FUR and LA feed [2,3], however, to the best of our knowledge, there are no reports on the use of combined FUR and LA feed to yield MTHF. Co-feeding FUR and LA to form MTHF is an attractive approach that will assist in the direct conversion of biomass to value-added chemicals since both FUR and LA can be co-produced from the cellulosic portion of the biomass.

Experimental/methodology. For the catalyst preparation, the alumina supports were synthesized using a sol-gel method and the metals were incorporated onto the support using the conventional impregnation method. For the hydrogenation reactions, both batch and continuous systems were utilized and the samples were analyzed using high performance liquid chromatography.

Results and discussion. The preliminary set of experiments investigated the types of feeds, feed ratios, and catalysts for the batch MTHF production. As depicted in Fig. 1a, complete conversion of the feed was attained for all the experimental runs but it can be observed that the main product varied from one type of feed to another. Interestingly, up to 55.0% yield of MTHF was achieved when FUR and LA was combined as feed. It can be assumed that the two reactions (FUR to 2-MTHF and LA to 2-MTHF) coexist in the reactor to produce 2-MTHF. Moreover, the feed ratio of 4:1 provided the highest MTHF yield (Fig. 1b), possibly due to the dominant presence of FUR in the feed that has prevented the formation of GVL, which is a highly stable intermediate in MTHF production. In addition, among the as-synthesized catalysts, the bimetallic Ni-Cu/Al_2O_3 catalyst showed the highest 2-MTHF selectivity which can be attributed to the synergistic effect of Ni and Cu as previously reported (Fig. 1c) [3].

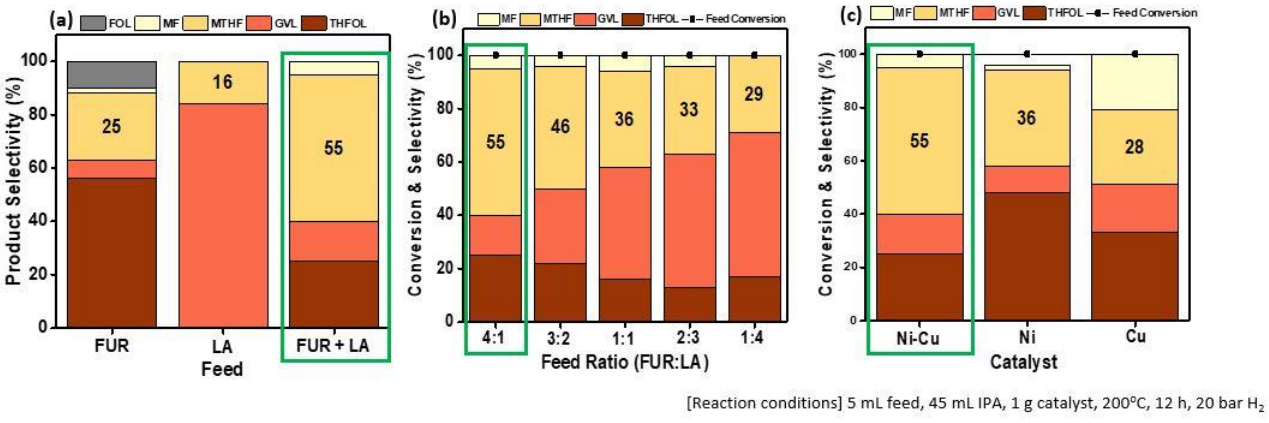

Figure 1. Results of the screening of the (a) type of feed, (b) feed ratio, and (c) catalysts.

Acknowledgments

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Rhenium-Catalyzed Production of Adipates from Aldaric Acids

M. Grilc*, F. M. Harth, B. Hočevar, and B. Likozar
[1] *Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia*
*miha.grilc@ki.si

Keywords: Adipic acid, Biomass conversion, Dehydroxylation, Deoxydehydration, Rhenium catalysts.

Introduction. Adipic acid and esters are crucial for polymer production, with millions of tons produced annually. The current method of production using petroleum-based feedstock leads to greenhouse gas emissions. Renewable methods using biomass, such as the catalytic dehydroxylation and hydrogenation of aldaric acids from lignocellulosic biomass, is a promising approach towards sustainable adipic acid production. This reaction has only recently evolved from a homogeneously to a heterogeneously catalyzed process making use of supported Re catalysts (Hočevar et al., 2021). Here we present how the properties of rhenium-based dehydroxylation catalysts and the process conditions influence the mucic acid conversion.

Experimental/methodology. Catalytic tests performed in stirred, heated autoclave reactors using mucic acid in methanol and solid catalysts (Re/C, Pd/C at 5 wt.-% metal loading, or bimetallic catalysts made via incipient wetness impregnation). All catalysts were pre-reduced under H_2 at 400°C. Tests were conducted at 120-175°C under N2 or H2, with 72 hour reactions and liquid samples analyzed by GC-MS.

Results and discussion. The selective dehydroxylation of mucic acid in yields > 90 % is possible at temperatures as low as 120 °C and without H_2 gas over monometallic Re/C (Figure 1-left). Methanol is both the reducing agent and protects the carboxyl functionality by esterification.

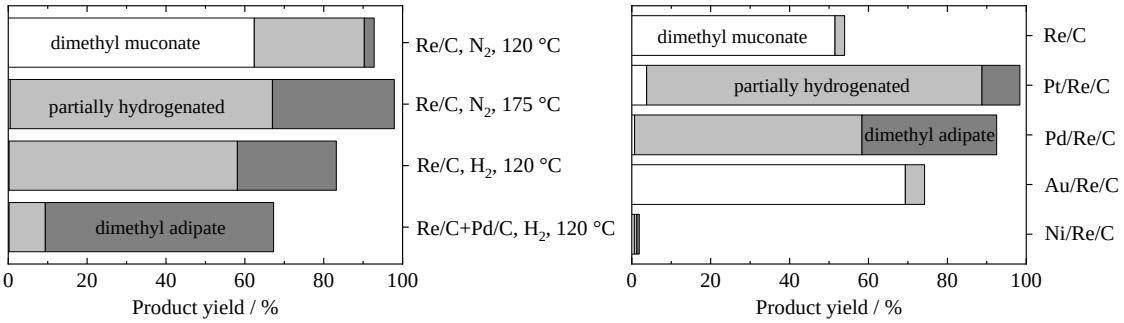

Figure 1. Product yields after 72 h in the dehydroxylation of mucic acid in methanol over a Re/C catalyst at different reaction conditions (left) and after 24 h over bimetallic catalyst at 120 °C under N_2 (right).

Deoxydehydration and hydrogenation of mucic acid derived from biomass can selectively produce adipates using rhenium-based catalysts. The reaction can be slow with the main product being dimethyl muconate. H_2 addition and increased temperature improve hydrogenation, while adding a hydrogenation catalyst like Pd/C can increase selectivity for dimethyl adipate up to 58%. Bimetallic catalysts of Re with noble metals (Pt and Pd) enhance activity and alter product distribution, with Pd/Re/C yielding 35% dimethyl adipate (Figure 1-right). Optimizing Pd loading and reaction time can achieve yields of up to 90%. Ni modification on the other hand is not suitable. To conclude, H_2-free production of dimethyl adipate with yields over 90% can be achieved through control of catalyst choice and reaction conditions.

Acknowledgments
This work was funded by the Slovenian Research Agency (ARRS) under core funding P2-0152 and project number J1-3020. Furthermore, funding from the Young Researchers Program from ARRS is acknowledged.

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Catalytic hydrodeoxygenation of phenolic compounds and lignin pyrolysis bio-oils towards drop-in aviation fuels

A. Margellou[1*], F. Zormpa[1], S. Torofias[1], A. Correa de Araujo[2], A. Funke[2], K. Triantafyllidis[1]
[1]*Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece*
[2]*Karlsruhe Institute of Technology, Institute of Catalysis Research & Technology, Eggenstein - Leopoldshafen, Germany; *amargel@chem.auth.gr*

Keywords: lignin pyrolysis oil, hydrodeoxygenation, non sulfided catalysts, aviation fuels

Introduction

Lignocellulosic biomass is an important source of renewable fuels and value-added chemicals. Lignin, which is a phenolic/aromatic macromolecule, can be converted to phenolic bio-oils via fast pyrolysis [1,2] and can be upgraded via hydrodeoxygenation (HDO) to aviation fuels (C_7-C_{12}). The aim of this study was the HDO of model phenolic compounds and mixtures, which simulate the light fraction of lignin pyrolysis bio-oils, with Ni-based bifunctional, non sulfided catalysts. Furthermore, the hydrotreatment/HDO of real thermal pyrolysis lignin bio-oils was also investigated.

Experimental/methodology

HDO experiments were performed in a high pressure batch autoclave reactor with hexadecane as a solvent and nickel (Ni) based catalysts supported on zeolites (ZSM-5, BETA, USY, etc.) and on mixed oxides/spinels, with different micro/mesoporous and acidic properties. Process optimization study included the effect of temperature, time, H_2 pressure, type of phenolic compound. Lignin bio-oils (obtained from fast pyrolysis of alkali lignin from Miscanthus on a twin-screw pilot-scale reactor) and hydrotreated samples were analyzed with GC-MS, GC-FID, 2D HSQC NMR, GPC and other tecnhiques. Catalysts were charcacterized by XRD, N_2 sorption, FTIR, TEM, XPS, acidity measurements, etc. before and after reaction.

Results and discussion

The model phenolic compounds were hydrodeoxygenated mainly towards cyclohexane and its isomer, methylcyclopentane. The fundamental reaction steps were identified by studying phenol HDO with 10%Ni/ZSM-5 (Si/Al=40), at a broad temperature range, ca. 140-250°C, and comprised of the cascade formation of cyclohexanone/cyclohexanol, cyclohexene, and finally cyclohexane and methylcyclopentane. At optimized mild conditions, such as 220°C, 1 hr, and 50 bar H_2 pressure, complete conversion of phenol was observed with up to 75% cyclo-alkanes. The effect of phenolic/aromatic ring substituent groups was then investigated, with the additional -OH (catechol) and methoxy (-OCH_3) groups (guaiacol) not affecting conversion/selectivity, reaching up to 85% yield of HDO products (cyclohexane, methylcyclopentane and 1,1-bicyclohexyl), over both small-micropore ZSM-5 zeolite and micro/mesoporous Beta zeolite. More complex/substituted rings, i.e., syringol, vanillin and 1,2,3-trimethoxybenzene, resulted in lower conversion and selectivity, with HDO product yields being lower than 30% over Ni/ZSM-5 catalysts, indicating space-restrictions considering the kinetic diameter of the feed compounds. The effect of intra-crystal mesoporosity of ZSM-5 and of the Brönsted to Lewis acid sites ratio of Beta zeolite was also investigated. Under the above optimized mild conditions, HDO of model mixtures consisting of alkoxy and alkyl phenols led to almost complete hydrodeoxygenation with products in the range of C_6-C_9, indicating also the ocurence of hydroalkylation reactions, in addition to the standard phenol HDO paths. When real lignin bio-oil feeds were tested, more intense temperature, time and pressure conditions were required, e.g. 280-350°C, 1-5 hrs and 50-90 bars H_2 in order to induce substantial deoxygenation of the contained mainly alkoxy/alkyl-phenols and heavier oligomers. Catalyst stability was also studied via characterization and reuse of spent materials, exhbiting high HDO efficiency (>95%), for at least three successive catalytic cycles. The metallic phase of Ni, as well as porous and acidic properties, were retained after use, as confirmed by XRD, XPS, BET and acidity tests, while coke formation was very low (<5 wt.%).

Acknowledgments

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Heterogeneous catalytic oxidation of furfural with hydrogen peroxide over a niobium catalyst

W.Y. Perez-Sena[1*], K. Eränen[1], A. Aho[1], T. Salmi[1], J. Wärnå[1], D. Murzin[1]

[1]*Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku, Finland*
[*]*wander.perezsena@abo.fi*

Keywords: Furfural, Hydrogen peroxide, Heterogenous catalysis, Niobia

Introduction. Selective oxidation of furfural with hydrogen peroxide offers a promising pathway (Fig. 1) to C4 chemical intermediates. Liquid-phase oxidation of furfural with hydrogen peroxide produces mainly 2-(5H)-furanone, succinic acid , malic acid, furoic acid and maleic acid. Formic acid is cleaved as a stoichiometric co-product in the oxidation. Both succinic and maleic acids can be dehydrated to their corresponding anhydrides at elevated temperatures. Numerous novel applications have been deduced for these molecules such as plant growth regulators, bactericides, and biodegradable plastics, e.g. polybutylene succinate, polyurethanes, plasticizers. Moreover, stoichiometrically efficient hydrogenation routes exist to upgrade them further to chemical intermediates, thus providing bio-based substitutes for these multimillion ton per year products, currently made almost entirely from fossil-based feedstock [1].

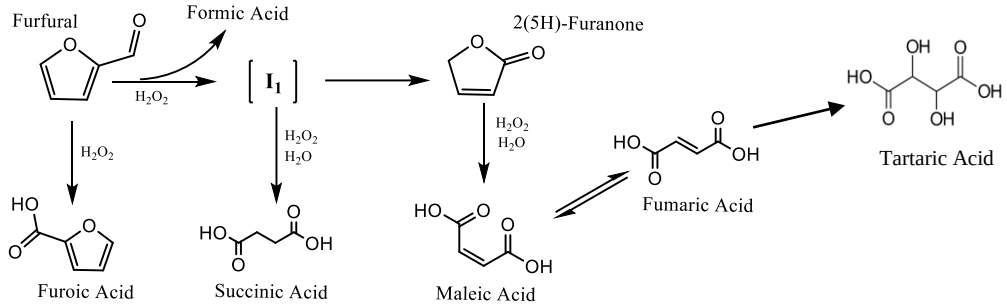

Figure 1. Simplified reaction scheme of furfural oxidation on niobium catalyst.

Experimental/methodology. The oxidation of furfural with hydrogen peroxide was studied in a 100ml jacked glass reactor under vigorous mechanical stirring at 50-90°C. Various niobium oxide catalysts were synthesized and screened. Multiple analytical techniques such as ^{1}H NMR, GC-MS, HPLC were applied for the identification and quantification of the final products. As for the characterization of the synthesized catalytic materials, relevant techniques such as HR-TEM, acidity, nitrogen physisorption, EDS and XPS were utilized in order to explain the catalytic reaction mechanism and the obtained results.

Results and discussion. Various niobium catalysts such as Nb_2O_5 (commercial), N_2O_5(meso), Nb-SBA-15 and Nb-SiO_2 were screened for the liquid-phase oxidation of furfural. It was evidenced that when a mesoporous niobium catalyst is used, the product selectivity of the system leans towards tartaric acid, instead of the typical products, e.g succinic and maleic acids. The formation of tartaric acid was observed to be independent of the amount of niobium deposited on the catalyst and rather influenced by the pore size and the acidity of the material as indicated by the results from the experiments using N_2O_5(meso) and Nb-SBA-15. The reaction mechanism was elucidated by performing independent experiments using maleic acid and fumaric acids as starting materials, and it was observed that the formation of tartaric acid mainly takes place through the oxidation of fumaric acid. The stability of the catalyst was tested by reusing the spent catalysts. Calcination at 450˚C was found to be necessary in order to regenarate the catalyst keep the level of conversion and yield constant in succesisve reaction cycles. The XPS analysis of the fresh, spent and regenarated catalyst revealed the oxidation state of niobium species during the stability test.

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Unveiling periodic trends and steering hydrodeoxygenation activity in biofuels production: experimental and computational approach

S. AlKhoori[1], A. Dabbawala[1], M. Harfouche[2], G. Siakavelas[3], A. Latsiou[3], S. Alareeqi[1], D. Anjum[1], S. J. Hinder[4], M.A. Baker[4], M. Khaleel[1], L. Vega[1], M. A. Goula[3], K. Polychronopoulou[1,2*]

[1]*Khalifa University of Science & Technology, Center for Catalysis and Separations (CeCaS), Abu Dhabi, United Arab Emirates*
[2]*Synchrotron-light for Experimental Science and Applications in the Middle East (SESAME), Al Salt, Jordan*
[3]*University of Western Macedonia, Koila, Greece*
[4]*University of Surrey, Guildford, United Kingdom*
[*]*Corresponding Author's E-mail address: kyriaki.polychrono@ku.ac.ae*

Keywords: Hydrodeoxygenation (HDO), Palm Oil, Zeolite Beta, Alkaline Earth Promoters, Periodic trends

Introduction. The global threats of environmental pollution and climate in the world have triggered the ongoing "low-carbon revolution," which reshapes the global energy market by lowering the significance of fossil fuels and boosting the reliance on renewable energy including biomass. Green biofuels are carbon-neutral renewable fuels derived from biomass that are converted to bio-oil through pyrolysis [1]. However, bio-oil is regarded as unsuitable for direct use in diesel engines and turbines due to its high oxygen and carboxylic acid contents. In this work, an experimental and theoretical investigations are carried out to elucidate the role of alkaline earth-metal promoters on biofuel production through palm oil HDO.

Experimental/methodology. The support used in this study, i.e., zeolite beta (Z-β) was supplied by ZEOLYST INTERNATIONAL (NH_4-form, SiO_2/Al_2O_3=25). Wet impregnation was followed for the support which was modified by different alkaline earth metalsas well as for the Ni introduction into the catalyst.

Results and discussion. Structural studies (XRD) display peaks of Z-β structure (JCPDS 48-0074) and Ni metal (JCPDS 01-070-1849), whereas as the cation's radii (Mg^{2+}< Ca^{2+}< Sr^{2+}< Ba^{2+}) increase, a decrease in zeolite peak intensity is observed and a concomitant broadening of Ni peaks due to the competitive growth of both metal/promoters' crystallites. The RGB mapping (HAADF-STEM analysis) of Mg-promoted catalyst suggests an even distribution of the metal (Ni^0) and the cation (Mg^{2+}) over Z-β matrix. Whereas for Ba-promoted catalyst, Ni particles are homogeneously anchored onto Z-βmatrix forming bigger agglomerates (23 nm) compared to Mg-promoted catalyst (17 nm), which can be justified by the segregation of Ba^{2+} species from the surface. Unveiling of the Ni localized environment was attempted using XANES. The normalized XANES results at the Ni K-edge (8333 eV) show a reduction in the absorption edge feature and an increase in the post-edge peak (EXAFS) with respect to Ni foil (reference), suggesting that Ni atoms were significantly oxidized, particularly in Mg-promoted catalyst. Based on the magnitude of the Fourier Transforms (FTs) of the EXAFS signals in R-space, the peak at ~2 Å represents the first Ni-Ni coordination shell, followed by two specific Ni-Ni interactions (3-5 Å). The peak centered at ~1.8 is attributed to Ni-O interaction. For all catalysts, the long-distance ordering and the features of crystalline structure are evidenced. The prepared catalysts were assessed for palm oil conversion; the highest conversion was obtained over 10Ni/5Sr-Beta catalyst (44 %) at 400 °C due to its moderate acid sites (NH_3-TPD) and higher Ni dispersion which promoted the electrophilicity of the catalyst and subsequently accelerated the adsorption of oxygenated molecules and activation of C-O bonds. Bader charge analysis indicate a periodic trend in the electronic transfer from Ni atoms to the promoters (i.e. Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}) indicating the close proximity of the constituents. The DFT studies were conducted over Ni(111) surface using palmitic acid as model compound due to the abundance of the latter in the palm oil. Different adsorption geometries were examined and the parallel dual-site adsorption of OH*hollow-hcp site of palmitic acid on Ni(111) surface was found to be the thermodynamically more favorable.

Acknowledgments

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Biofuels production via hydrocracking of hydrothermal liquefaction biocrude oil and lignocellulosic pyrolysis oil

A. Dimitriadis[1], N. Tourlakidis[1], G. Meletidis[1], S. Bezergianni[1]

[1]*Centre for Research & Technology Hellas (CERTH),*
Chemical Process and Energy Resources Institute (CPERI) Thessaloniki, 57001, Greece
[*]*adimitr@certh.gr*

Keywords: Biofuels, hydrocracking, biocrude oil, pyrolysis oil, hydrothermal liquefaction

Introduction.
Biomass pyrolysis and hydrothermal liquefaction (HTL) are two comparable technologies, as they both render bio-based intermediate products (often referred to as pyrolysis oil and biocrude oil respectively) [1]. However, both products from pyrolysis and hydrothermal liquefaction required further upgrading to enable its end-use as fuel as well as its compatibility with the corresponding combustion systems [2]. Catalytic hydrotreatment (HDT) of pyrolysis oil as well as biocrude oil allowing stabilization and deoxygenation is considered the state-of-the-art technology [3]. To that aim the current work targets to investigate the HDT upgrading of both pyrolysis oil as well as HTL biocrude oil.

Experimental/methodology.
The upgrading of both feeds was tested on the same operating window, utilising the same commercial hydrotreating catalyst (NiMo) in order to find out which feed will render the highest quality liquid fuels and how will affect the catalyst performance. Three operating conditions were investigated with both feeds. The aim was to investigate the effect of hydrotreating temperature as well as the effect of H_2/oil ratio on product quality and yields of the process. The HDT experiments were performed in the small-scale continuous flow pilot plant TRL 3 of CERTH.

Results and discussion.
The results have shown that hydrotreating of both pyrolysis oil and biocrude oil leads in a two-phase liquid product that consists from the organic phase and the aqueous phase. The aqueous phase is formed via the decarboxylation and dehydration reactions, which is a typical side product of biomass catalytic hydrodeoxygenation. For both feeds, it was found that the optimum operating condition is at 330°C, 1000 psi, LHSV 1hr^{-1} and 5000 scfb H_2/oil ratio. From the comparison of the two products, it was found that the product from biocrude oil has lower density (0.841 g/ml) fulfill diesel specifications (0.80-0.85 g/ml), lower viscosity (5.3 cSts), higher cetane number (56, fulfill diesel specifications >51) and higher organic phase yields (organic yields: 65.5%wt), compared to the HDT product of pyrolysis oil (density: 0.92 g/ml, viscosity: 9.0 cSts, cetane index: 35, organic yields: 59.5 wt%).

Acknowledgments
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The key to obtain a high yield of renewable jet fuel from hydroprocessing of fatty acids and esters

Asbjørn S. Andersson[1*], Uffe V. Mentzel[1], Rasmus G. Egeberg[1]

[1]*Topsoe, Lyngby, Denmark*
[*]*assa@topsoe.com*

Keywords: Sustainable Aviation Fuel, Renewable Jet Fuel, HEFA-SPK, dewaxing, isomerization
Introduction. Sustainable Aviation Fuel (SAF) is a prerequisite for low-carbon travel. Industry players, passengers, and the planet will all benefit. SAF can be produced by different processes and from various feed stock types and Topsoe offers technology solutions for multiple pathways. In this study the focus will be on converting triglycerides or fatty acids into renewable jet fuel.
Experimental/methodology. Results from hydroprocessing pilot plant studies reacting both real feed and model feed over a fixed catalyst bed will be discussed.
Results and discussion. In order to convert fatty acids and esters into renewable jet fuel the feed stock needs to undergo various types of chemical reactions, like hydrodeoxygenation (HDO), hydroisomerization (HI), and hydrocracking (HDC). Detailed knowledge and control of these reaction mechanisms is key to design a process, that will produce a high yield of renewable jet fuel meeting the ASTM D 7566 specification.

The catalytic reaction with hydrogen to remove oxygen from fatty acids or esters results in mixture of normal alkanes with a melting point point above room temperature. To be used as jet fuel the freezing point needs to be lowered to -40°C or below, which can be achieved by using a hydroisomerization catalyst. Other property requirements like density and distillation curve are also playing a key role in how to balance the different reaction types and to meet these requirement it is also necessary to do some conversion by hydrocracking.

While the boiling point decreases with increasing degree of isomerization, the effect on density is not as unequivocal. Thus, it would be quite attractive to find a catalyst that can do isomerization and density reduction without a high yield loss due to cracking. Data from pilot plant testing of several catalyst formulations will be presented and the results discussed. The effect of the two different HDO pathways[1] leading to either even-numbered alkanes or uneven-numbered alkanes will also be discussed with respect to the consequence on jet yield and density.

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Optimization in the deoxygenation of m-cresol by creating Ni-Nb interfaces

Camila A. Teles[1,*], Carmen Ciotonea[2], Sébastien Royer[3], Frédéric Richard[1]

[1] *Université de Poitiers, CNRS, Institut de Chimie des Milieux et Matériaux de Poitiers, UMR 7285, rue Michel Brunet, BP633, 86022 Poitiers, France.*

[2] *Université du Littoral Côte d'Opale, Unité de Chimie Environnementale et Intéractions sur le Vivant-UCEIV, UR4492, SFR Condorcet FR CNRS 3417, 59140 Dunkerque, France.*

[3] *Université de Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France.*

[*] *camila.abreu.teles@univ-poitiers.fr*

Introduction. The hydrodeoxygenation (HDO) reaction of m-cresol, a model molecule representative of the lignin-derived bio-oil, is strongly affected by the type of catalyst. Hydrogenation of m-cresol yielding oxygenated compounds such as ketone and alcohol is promoted by supported metals while deoxygenation toward toluene can be promoted by a metal-oxophilic site interface [1]. C-C hydrogenolysis can also takes place by using metals such as Ni [2]. In this work we studied the effect of the interfacial sites between Ni particles and NbO_x species to promote deoxygenation and minimize hydrogenolysis, by preparing a series of Ni-NbO_x dispersed on SBA-15 catalysts and testing in the HDO reaction of m-cresol at gas phase.

Experimental/methodology. SBA-15 was prepared by conventional templating method. The Ni-Nb/SBA-15 samples, varying the content of Ni and Nb between 2.5-5 wt.% were prepared by melting infiltration method, followed by thermal treatment at 500 °C for 6 h. The samples were characterized by N_2 physisorption, XRD, H_2-TPR, STEM and IV-pyridine. The HDO of m-cresol was performed in a fixed-bed reactor operating at 300 °C and atmospheric pressure. The catayst were reduced *in situ* at 500 °C, 1 h, under pure H_2 flow before reaction. Reactant and reaction products were analyzed by gas chromatography.

Results and discussion. By comparing the product distribution obtained at low level of conversion for all catalysts, important differences were observed depending on the catalyst composition. Oxygenated produts such as 3-methylcyclohexanone and 3-methylcyclohexanol (50 and 19 % of selectivity, respectively) were the major products obtained over Ni/SBA-15, with minor production of toluene (22 %) and phenol (6 %). By introducing niobium to the catalyst, the selectivity to these oxygenated products continuouly decreased while increasing the selectivity to deoxygenated products such as toluene, methylcyclohexenes and methylcyclohexane, with a maximum being observed for a catalyst containing a Nb/Ni molar ratio of 1 (72 % of toluene, 12 % of methylcylohexenes and 6 % of methylcyclohexane). Besides that, phenol is not further detected. The formation of such products can be explained by three main reaction routes: (i) the direct deoxygenation (DDO) to yield toluene, (ii) hydrogenation (HYD) of the aromation ring yielding the ketone and alcohol followed by dehydration to the alkanes which may be further hydrogenated to the respective alkane, and (iii) hydrogenolysis (HYG) of the methyl group yielding phenol. The addition of Nb close to the Ni particles, as evidenced by the characterization results, significantly increased the DDO rate up to 7-fold while eliminating the hydrogenolysis pathway (Figure 1). Thus, the results clearly evidenced that deoxyenation of m-cresol over Ni-based catalysts can be optimized by creating interfacial sites with oxophilic species such as NbO_x.

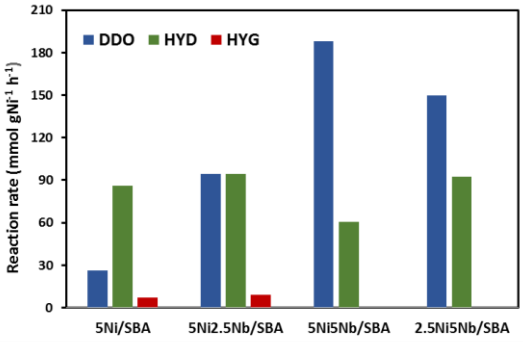

Figure 1. Reaction rates for the different reaction routes as a function of catalyst composition.

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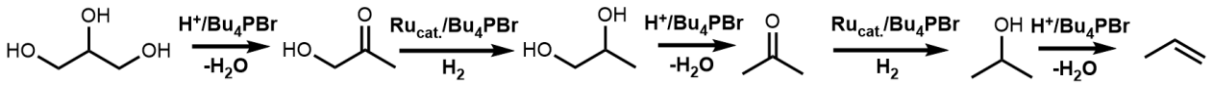
Bio-Olefins from Crude Industrial Waste Glycerol and Sugar Alcohols *via* Ru-Catalyzed Hydrodeoxygenation in Ionic Liquids

Kwinten Janssens[1*] and Dirk E. De Vos[1]

[1]*Centre for Membrane Separations, Adsorption, Catalysis and Spectroscopy, KU Leuven, Leuven, Belgium*
[*]*kwinten.janssens@kuleuven.be*

Keywords: Biomass, Waste Valorization, Sugar alcohols, Hydrodeoxygenation, Ionic Liquids

Introduction. Due to the high oxygen functionality of biomass, the valorization of renewable substrates to valuable chemicals typically requires deoxygenation reactions, such as deoxydehydration (DODH) or simple dehydration. We hypothesized that if a fast dehydration (by the Bu_4PBr IL) is combined with exclusive hydrogenation of C=O bonds, even in the presence of C=C bonds, the overall sequence may result in the stepwise deoxygenation of a sugar polyol to a bio-olefin, as a kinetically stable end product. By using H_2 as a reductant, this is essentially a hydrodeoxygenation (HDO), which would be formally similar to, but a more atom efficient, greener complement to the classical DODH (using PPh_3). [1] In this work we successfully converted **crude biowaste glycerol** directly into **biopropylene in high yield (82%) and olefin selectivity (94%)** carefully avoiding overhydrogenation.[2] Next, a series of more complex, economically relevant sugar alcohols (erythritol, xylitol and sorbitol) were converted to their respective mono-olefins.[3] CO was discovered to be crucial to maintain high catalyst stability over multiple cycles, this was confirmed using advanced X-ray Absorption Spectroscopy (XAS) at the European Synchrotron Radiation Facility (ESRF).[4]



Experimental/methodology. All reactions were performed in a 10 mL custom-build pressure reactor. A simple pretreatment step with a CO source was performed prior to the catalytic reactions. After each reaction, the mixture is cooled and spontaneous product separation occurs: the catalyst and ionic liquid solidifies and the olefin products are easily extracted in an apolar dodecane layer, quantified *via* GC/GC-MS. Catalyst characterization was based on *in-situ* XANES and EXAFS measurements performed at ESRF in Grenoble (BM23) and Soleil in Paris (SAMBA).

Results and discussion. Intensive screening of different hydrogenation catalysts has led to the discovery of homogeneous Ru catalysts resulting in high olefins selectivities, rather than overhydrogenation to the alkane. It was hypothesized that this was a result of the formation of a stable Ru-Carbonyl-Halide complex, in multiple ways, e.g. through pretreatment with CO gas [2], *in-situ* decarbonylating of aldehyde intermediates or *via* controlled thermal decomposition of formaldehyde [3]: All resulting in small partial pressures of CO which are essential to form the desired Ru-hydrogenation complex. The different steps in the formation of the active catalyst were characterized at ESRF to get *in-depth* insights in the Ru environment, confirming changes for both Ru-Halide and Ru-CO interactions.[4] In order to tolerate common waste stream impurities (Water, MeOH, NaCl) found in crude glycerol from *ex-biodiesel* saponification, again CO pretreatment proved to be crucial in maintaining catalyst stability and selectivity over 8 cycles.[2] In addition, the catalyst applicability was extended to other **biobased sugar alcohols**: erythritol, xylitol and sorbitol. All were converted selectively to their respective **mono-alkenes (>95% olefin selectivity)**.[3] To the best of our knowledge, this is the first report of the successful conversion of these higher polyols to mono-alkenes.

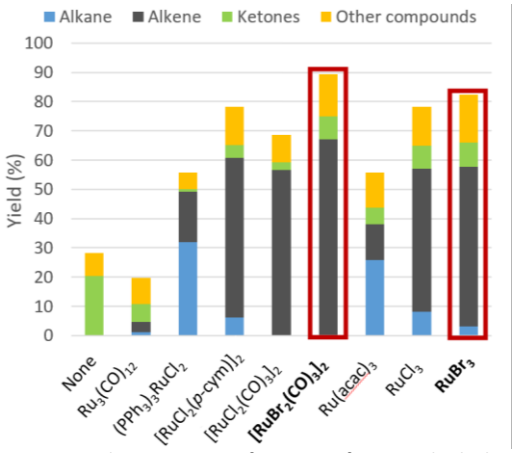


Fig.1: Catalyst screening for HDO of Sugar Alcohols

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Optimization of catalytic system and process conditions for the oxidation of bio-based HMF solution in batch and continuous flow

D. Neukum[1], E. Saraçi[1,2], L. Baumgarten[1], D. Wüst[3], B. B. Sarma[1,2], A. Kruse[3], J.-D. Grunwaldt[1,2*]

[1]*Institute of Chemical Technology and Polymer Chemistry, KIT, Karlsruhe, Germany*

[2]*Institute of Catalysis Research and Technology, KIT, Eggenstein-Leopoldshafen, Karlsruhe, Germany*

[3]*Institute of Agricultural Engineering, University of Hohenheim, Stuttgart, Germany*

[*]*dominik.neukum@kit.edu; grunwaldt@kit.edu*

Introduction. The production of bio-based monomers is a constantly growing field in industry and academia.[1] The synthesis of 2,5-furandicarboxylic acid (FDCA) from 5-(hydroxymethyl)furfural (HMF) is particularly interesting due to the high quantity of possible bio-based feedstocks for HMF production, like cellulose or inulin.[2] The state-of-the-art heterogeneous catalysts for this oxidation process are based on noble metals. However, the use of biomass for the production of FDCA is still a challenge due to its complex nature. To decrease costs and increase the sustainability of FDCA production, all stages of its production have to be optimized with minimal intermediate purification steps and biomass waste, e.g. chicory roots, should be used. To accomplish this, we have studied the influence of by-products in bio-based solutions on the catalysts and optimized the catalytic system accordingly.[3,4] We aim to develop an efficient process for FDCA production by improving the reaction conditions and process design (Fig. 1).

Experimental/methodology. Noble metal (Au, Pt, Pd, Ru) based catalysts supported on carbon black were prepared by supporting priorly prepared colloids or by impregnation method. The catalysts were characterized in detail by X-ray diffraction, X-ray absorption spectroscopy, electron microscopy and optical emission spectrometry. The oxidation of pure and bio-based HMF solution was performed in aqueous phase using Na_2CO_3 as base and air as oxidant in batch autoclaves as well as in a continuous flow reactor.

Results and discussion. The oxidation of HMF solution derived from saccharides was optimized in terms of catalyst composition and process conditions. We found an influence of amino acids deriving from the chicory roots on the oxidation process leading to poisoning of the catalysts. The influence of key amino acids on Au-, Pt-, Pd- and Ru-based catalysts was systematically investigated. Particularly, cysteine and cystine poisoned the catalysts at concentrations in the range of µg mL^{-1}. Based on these results, we combined the more stable Pd with the highly active Au in order to obtain an active and robust catalyst. The AuPd alloy outperformed all monometallic catalysts and led to an improved tolerance against sulfur containing compounds. Moreover, we optimized the reaction conditions (T, p, base equivalents) with bio-based HMF solution to minimize the catalyst mass and at the same time achieve an FDCA yield >90%. In addition, we tested higher HMF concentrations in the bio-based feedstock, since high dilution of HMF is often seen as a drawback. Optimization of the base dosage was the key to increasing the FDCA yield leading us to the implementation of a two-step process to enable higher concentrations. Finally, we tested the AuPd-based catalyst in continuous flow oxidation of pure and bio-based HMF solution to investigate on a further improvement of the process design. Continuous operation renders the process more sustainable and economical by avoiding catalyst separation and process interruption between each batch. The identification of critical compounds in bio-derived solution, improvement of the catalyst system and optimization of reaction conditions, allow the development of an efficient process for the production of FDCA monomer from chicory root. This study emphasizes the importance of systematically investigating and rationally optimizing each step to make the overall process feasible for the use of bio-based feedstock.

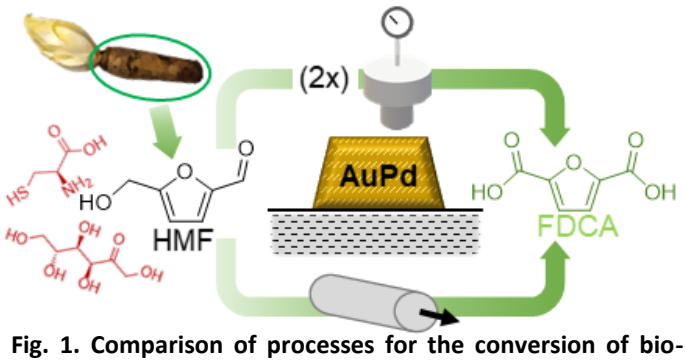

Fig. 1. Comparison of processes for the conversion of bio-based HMF to FDCA.

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Polyoxometalate based catalysts for the oxidative hydrolysis of cellulose to glycolic acid

A. K. Beine[1*], Z. Li[2], X. Yi[3], R. Palkovits[4], C. Liu[5], X. Wang[2]

[1] *Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany*
[2] *Northeast Normal University, Changchun, P. R. China*
[3] *Changchun Institute of Applied Chemistry, Changchun, P. R. China*
[4] *RWTH Aachen University, Aachen, Germany*
[5] *Beihua University, Jilin City, P. R. China*
[*] *katharina.beine@cec.mpg.de*

Keywords: Polyoxometalates, thermomorphic catalyst, glycolic acid

Introduction. Polyoxometalates (POMs) have been identified as promising catalysts for both acid catalysed hydrolysis and retro-aldol reactions as well as metal catalysed oxidation.[1] Their Brønsted acidity and redox activity can be tuned depending on the composition of the POM. Due to the good solubility of POMs in water and organic solvents, recycling strategies are needed to design industrially applicable processes. In our work, we have investigated the oxidative hydrolysis of cellulose to the value-added product glycolic acid (GA), which finds application in the pharma and food industry. Complexation of the most promising POM with a suitable ionic liquid allows the complete recycling of the catalyst.

Results and discussion. The POM $H_3PMo_{12}O_{40}$ (H_3PMo) was tested among others in the homogeneously catalysed oxidative hydrolysis of cellulose where it outperformed the other POMs yielding 52 % GA at 80 % conversion. Formic acid (FA), 5-hydroxymethylfurfural (5 HMF) and C_6-sugars were obtained as side products. To be able to recycle the catalyst we prepared assemblies of H_3PMo with the ionic liquid MIMPS which show a thermo-responsive behaviour (i.e. the catalyst is immiscible with water at RT, but dissolves completely in water at reaction temperature (> 60°C)). Different amounts of MIMPS were used to replace either one, two or all three acidic protons of the H_3PMo resulting in $[MIMPS]_xH_{3-x}PMo$ materials. Compared to the completely homogeneous H_3PMo, a similar activity and selectivity was found for $[MIMPS]H_2PMo$ (Figure 1). The main product GA was formed with a yield of 51% and a conversion of 82% was reached. With increasing substitution of protons by MIMPS yield and activity decrease. MIMPS itself is moderately active in the conversion, which can be explained by its minor Brønsted acidity. A successful recycling of the catalyst with minor loss of activity over 5 runs could be shown.

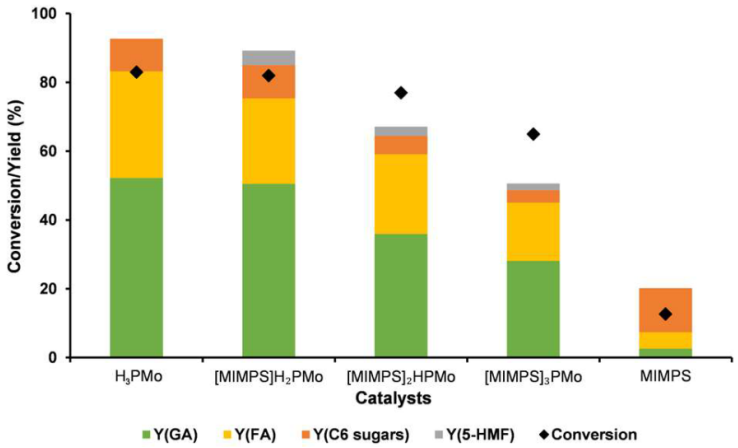

Figure 1: Effect of H_3PMo, $[MIMPS]_xH_{3-x}PMo$ and MIMPS on the oxidative hydrolysis of cellulose. Reaction conditions: 0.1 g cellulose, 150 °C, 0.06 mmol catalyst, 1.0 MPa O_2, 8 h.

Conclusion. H_3PMo was identified as promising catalyst for the oxidative hydrolysis of cellulose, which can be solidified by complexation with the ionic liquid MIMPS resulting in a thermo-responsive catalyst showing molecular activity and selectivity. The recyclability of $[MIMPS]H_2PMo$ was shown over 5 consecutive runs confirming its high potential as multifunctional catalyst in different sustainable conversions.

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Oxidation of cyclohexane to KA oil using noble metal-free Ce and Zr-based mixed oxides

Alessandro Vomeri[1*], Marta Stucchi[1], Ana B. Hungria[2], Jose J. Calvino[2], Laura Prati[1]

[1]*Università degli Studi di Milano, Milan, Italy*
[2]*Universidad de Cádiz, Puerto Real, Spain*
[*]*alessandro.vomeri@unimi.it*

Keywords: KA oil, cycloehaxane oxidation, mixed oxides, inverse microemulsion, heterogeneous catalysis.

Introduction. Cyclohexane oxidation is a key reaction of industrial chemistry as KA oil (a mixture of cyclohexanol and cyclohexanone) is the starting point for the industrial production of nylon-6 and nylon-6,6. However, the reaction presents kinetic and thermodynamic difficulties and proceeds through a complex free radical mechanism. The current industrial process is performed in the presence of homogeneous Co-based catalyst and limits conversion of cyclohexane in order to maintain a relatively high selectivity to K-A oil (around 80% at 4-5% conversion)[1]. In the past years, many heterogeneous catalysts have been studied, such as metal (Au, Ag, Co, V, Fe, Cr, Ti, etc.) supported on oxides, carbons, mesoporous materials and metallorganic structures[2,3]. In this work, a series of non-noble metal (Cu, Fe) Ce and Zr-based mixed oxides, prepared by inverse microemulsion, have been shown to be active in cyclohexane oxidation and open the way to a new class of active catalysts for this reaction.

Experimental/methodology. The preparation of the mixed oxides was carried out by inverse microemulsion[4] in order to obtain Ce or Zr mixed oxides containing either Cu or Fe in a lower amount (1:9 molar to the amount of Ce or Zr). A bare Ce-Zr mixed oxide with 1:1 molar ratio was also prepared. These mixed oxides were reduced in the presence of $NaBH_4$ at 300°C in order to introduce defects in the structure of the oxides. The bare oxides and the reduced ones were tested in the catalytic oxidation of cyclohexane at 120°C and 4 bars of O_2, using benzaldehyde (10 uL) as radical initiator, as in our previous work[5]. The catalysts were charcaterized by different solid-state analytical techniques, such as STEM/EDX, XRD, BET and XPS.

Results and discussion. The prepared materials show better productivity per hour than many of the best state-of-the art catalysts mentioned in a recent 2022 review[6]. Among those, no catalyst outperforms ours at comparably mild reaction conditions (120°C, 4 bar O_2) or avoiding the use of expensive radical initiators (TBHP, H_2O_2) or the use of noble metals. We found that Ce-based oxides in general behaved better than Zr-based ones. Selectivity control was noticed in Cu-containing bare oxides, which resulted in favouring the more industrially valuable cyclohexanone[7] giving a K/A>1.5, while the other oxides gave a K/A<1. Reducing the mixed oxides, thus introducing some defects and reducing the metals, the Zr-based ones boosted up their activity. The behaviour before and after reduction differs greatly for Cu or Fe containing oxides and this has been correlated with some structural modification. Indeed, studying the variation in the mixed oxides composition (STEM/EDX), lattice parameter (XRD) and oxidation states (XPS) due to the reduction step, we found correlation between the changes in composition and lattice parameter and the resulting productivity. Therefore, Cu and Fe modified Ce and Zr- mixed oxides represent an attractive discovery in terms of ease of preparation, effectiveness and stability.

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The dehydration of fructose to 5-HMF over hierarchical USY zeolites: mechanistic aspects and catalyst optimization

Y. Han, K. Larmier, G. Pirngruber*
IFP Energies nouvelles, Solaize, France
**gerhard.pirngruber@ifpen.fr*

Introduction. 5-HMF is a very important intermediate for the production of biomass-based products. It is obtained by Bronsted acid catalyzed dehydration of fructose. Selectivity is a big issue: the formation of by-products (humins) resulting from oligomerization reactions must be avoided [1]. Large pore zeolites are promising candidates as heterogeneous catalysts, but even 12MR pore systems might encounter diffusion problems in the conversion of bulky sugar molecules. In our study we first evaluated a series of commercial USY zeolites with varying acidity and mesoporosity. We then modified the acidity and porosity of the USY zeolites by acid and base treatments, in order to optimize their activity and selectivity.

Experimental. The conversion of fructose by zeolite catalysts was carried out in DMSO solvent (in order to inhibit Lewis acid catalyzed reactions) at 95°C. The products were analyzed by HPLC and NMR. For introducing hierarchical porosity in USY zeolites a base treatment with tetralkylammonium hydroxide was employed (0.2 M, 65°C, 2h), if necessary preceded by a dealumination step with oxalic acid.

Results and discussion. Some of the commercial USY zeolites were active and selective catalysts for the production of 5-HMF from fructose. 5-HMF was not a primary product; it only appeared after a short induction period. By dedicated experiments with labelled fructose we could identify the intermediates on the pathway to 5-HMF [2]. Quite surprisingly, the 5-HMF production rate was anti-correlated with the concentration of Bronsted acid, but increased with increasing mesopore volume of the zeolite (Figure 1). We, therefore, decided to explore USY catalysts with increased mesopore volume, obtained by desilication with a base. USY zeolites are quite sensible to base treatment and easily loose crystallinity, unless organic protecting agents are added during the treatment. They impede amorphisation by adsorbing on the pore surface. We tested tetralkylammonium cations of different chain lengths, from C1 to C4, as protecting agents. Methyl had a weak protecting effect. It generated high mesopore volumes, but also led to significant amorphisation of the zeolite structure. On the other extreme, butyl had a strong protecting effect and, thus, limited the mesopore formation. The best compromise was found with tretrapropylammonium hydroxide. The Si/Al ratio of the zeolite also played an important role. Zeolites with low Si/Al ratio were quite inert during the base treatment, while high Si/Al ratios easily amorphised. The optimal range of Si/Al for applying the base treatment was between 16 and 27 (Figure 1c).

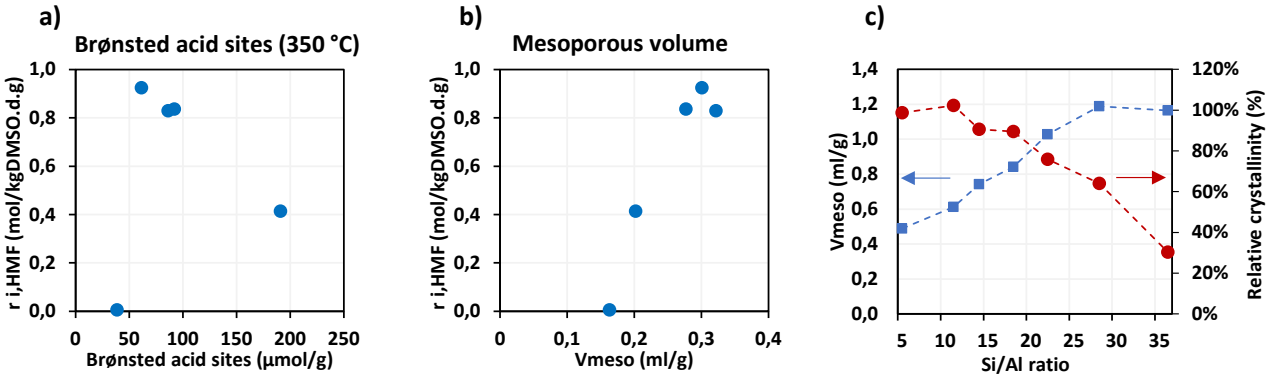

Figure 1 Rate of 5-HMF production as function of a) Bronsted acid site concentration and b) mesopore volume of commercial USY zeolites. c) Compromise of mesopore volume vs crystallinity.

The hierarchical USY zeolites were tested in the conversion of fructose and showed surprising results. If a gain in mesoporosity was obtained by sacrifying crystallinity, the activity was low. At constant mesopore volume, increasing the Bronsted acid site concentration had a detrimental effect on activity. We are currently investigating whether this is related to an increase in hydrophilicity, leading to inhibition by H_2O generated during the reaction. Still, a minimum concentration of Bronsted acid sites remains indispensable; increasing mesoporosity is beneficial if it increases the accessibilty of Bronsted acid sites.

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Selective Hydrodeoxygenation of Palm Fatty Acid Distillate to Produce *n*-Paraffin with Even Carbon Number

E. W. Qian*, T. Simomura, K. Kamiya

Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Nakacho 2-24-16, Koganei, Tokyo 184-8588, Japan
**whqian@cc.tuat.ac.jp*

Keywords: hydrodeoxygenation, nickel catalyst, solid acidic support, phase change material

Introduction. Linear even number hydrocarbons (*n*-C_{16} and *n*-C_{18}) as phase change material (PCM) can be produced via selective hydrodeoxygenation (HDO) of vegetable oil and suppression of other side reactions. It was reported that the conventional hydrotreating sulfided Mo/Al_2O_3 catalysts with a little addition of Co showed high selectivity toward the hydrodeoxygenation (HDO) pathway [1]. Additionally, the selectivity could be controlled by using the acidic zeolite supports, e.g. SAPO-11, HBeta and ZSM-22 [2-4]. Also, the addition of P to the Ni catalyst [5] or the use of a bimetallic Mo- Ni catalyst [6] can promote significantly the HDO pathway. How to selectively obtain even hydrocarbons have not been clarified. Hence, in this study, the influence of several acidic support on the formation of the active phase on Ni-based catalyst, the reaction pathway and the yield of *n*-paraffin was investigated. In addition, the addition effect of the promotor on Ni catalysts and reduction condition were also investigated.

Experimental. Ni based catalysts were prepared by impregnation method using Al_2O_3, SAPO-11 and H-Beta etc. These samples were characterized by using BET, pyridine FT-IR, CO chemisorption, XPS and H_2-TPR. Their catalytic performance in hydrotreating of methyl laurate and Palm Fatty Acid Distillate (PFAD) were tested by using a fixed-bed flow reactor system. The reactions were conducted at different temperatures (275–375 °C) and under 3 MPa. The liquid products were analyzed using GC-FID and GC-MASS.

Results and discussion. Ni/HBeta and Ni/SAPO-11 demonstrated higher activity and isomerization selectivity than Ni/Al_2O_3 due to the presence of the Brønsted acid on the supports. In addition, Ni/HBeta and Ni/SAPO-11 showed higher selectivity of *n*-C_{12} at 275 °C and 300 °C, respectively. Ni/Al_2O_3 showed lower *n*-C_{12} selectivity than the zeolite catalyst due to its lower activity compared to other catalysts, and increased cracking selectivity due to its large pore size. Consequently, it was concluded that Brønsted acid affect the formation of Ni^0 species which is related with activity of the catalyst; however, it also promoted the isomerization and cracking reactions. Further, Comparing with Ni/ALPO-11, Ni/SAPO-11 showed higher deoxidation activity and selectivity to *n*-C_{12}.

The addition effect of various promoters such as Fe, Ru, W, Mo and Re etc. on Ni/SAPO-11 was investigated. The addition of the promoter inhibited cracking and isomerization. Comparing with other promoter, the addition of Mo onto Ni/SAPO-11 significantly resulted in increasing selectivity to *n*-C_{12} because of modification to adsorption mode of methyl laurate onto HDO active site. Further, the addition amount of Mo to Ni/SAPO-11 catalyst was optimized. It was found that NiMo/SAPO-11 catalyst with Ni/Mo=8 showed the highest selectivity to *n*-C_{12}. It is suggested that the addition of Mo enhanced the reduction of Ni; and the presence of a little amount of MoO_x (x<3) inhibited the decarbonylation reaction (formation of C_{11}) via changing adsorption mode of methyl laurate on to HDO active sites. Also, it was found that the conversion of methyl laurate and selectivity to *n*-C_{12} on NiMo/SAPO-11 catalyst increased with increasing reduction temperature from 400°C to 550°C due to the formation of Mo^{4+} and Mo^{5+}.

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Enzymatic Epoxidation of Fatty Acids: Catalysis, Kinetics and Process Intensification by Acoustic Irradiation

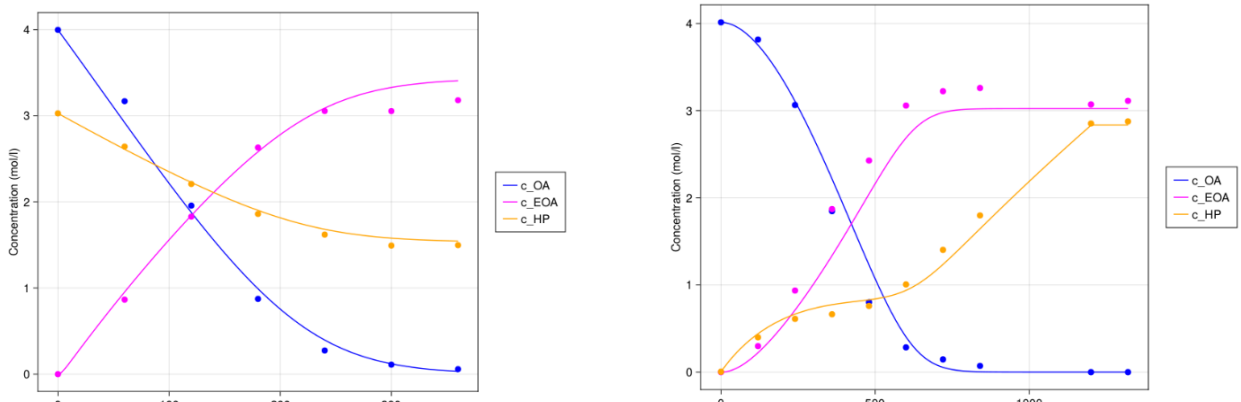
T. Salmi[1], A. Freites Aguilera[1], W. Wikström[1], P. Lindroos[1], P. Tolvanen[1], K. Eränen[1]*

[1]Åbo Akademi, Johan Gadolin Process Chemistry Centre (PCC), Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Turku/Åbo, FI-20500, Finland
** tapio.salmi@abo.fi*

Introduction. Northern Europe and Canada are the countries of intensive utilization of forest biomass. The main use of biomass is the production of pulp and paper via the Kraft process, which implies that lignin and most part of hemicelluloses are dissolved in alkali under elevated temperatures, whereas cellulose fibers remain in solid form. A very valuable side product of Kraft pulping is tall oil, which consists of fatty acids, e.g. oleic, linoleic, linolenic and abietic acids. In developing the most modern biorefineries, a further refinement of the tall oil fatty acids (TOFA) is an acute issue. Epoxidation of unsaturated fatty acids with hydrogen peroxide is an attractive alternative, since epoxidized fatty acids and fatty acid esters can be used as intermediates for biolubricants, plasticizers, biobased rigid foams and non-isocyanate polyurethanes. The classical technology for fatty acid epoxidation is an indirect process requiring a reaction carrier, such as formic or acetic acid, which reacts with hydrogen peroxide giving a percarboxylic acid as the real epoxidizing agent. This complicated multiphase process has a safety risk because of the appearance of percarboxylic acids. Therefore, the direct epoxidation of fatty acids in the presence of an immobilized enzyme is an attractive green and safe pathway to epoxidized fatty acids. The main challenge is to find a catalyst for direct epoxidation. Enzymatic epoxidation was investigated in this work, including kinetic experiments, process intensification with the aid of acoustic irradiation and very detailed kinetic modelling.

Experimental/Metholology. Immobilized lipase *Candida Antarctica* lipase B on an acrylic resin support (Novozym® 435, Novo A/S) was used as as the catalyst and aqueous hydrogen peroxide as the epoxidation agent. Extensive kinetic and catalyst stability studies were conducted in a jacketed laboratory-scale glass reactor, which was operated both in batch and semibatch modes: hydrogen peroxide was added to the reaction mixture either instantaneously or gradually. Intensive stirring was applied to maintain the oil-in-water system. The reactor was equipped with an ultrasound stick to investigate the effect of acoustic irradiation on the reactant conversion and product selectivity. The reactant molar ratio, temperature, stirring rate and hydrogen peroxide addition policy were the experimental parameters. The concentrations of epoxide groups and double bonds were determined by titrimetric analysis and the ring-opening products were identified by proton NMR. The catalyst morphology was investigated by SEM.

Results and discussion. The experimental results showed that almost complete conversions of the double bonds in oleic acid are achievable in isothermal batch and semibatch operation conditions, with low concentrations of ring-opening by-products formed. Ultrasound irradiation enhanced the rate and retarded the catalyst deactivation, and higher oleic acid conversions were reached compared to silent conditions. Kinetic modelling of the experimental data was based on the following stoichiometry: A + H = B + W, A+ B = R + A where A= oleic acid, H= hydrogen peroxide (HP), B=peroleic acid, W= water, R= epoxide. The adsorption and desorption steps in the reaction mechanism were assumed to be rapid, whereas the surface reaction steps were taken as rate determining. Rate equations for the formation of peroleic acid and epoxide were derived and the numerical values of the kinetic and adsorption parameters were estimated with non-linear regression analysis. The model equations (ODEs) were solved numerically. The model gave a very good fit to the experimental data as illustrated below (left: batch, right: semibatch operation; blue: oleic acid (OA), yellow: hydrogen peroxide (HP), magenta: epoxidized oleic acid (EOA).

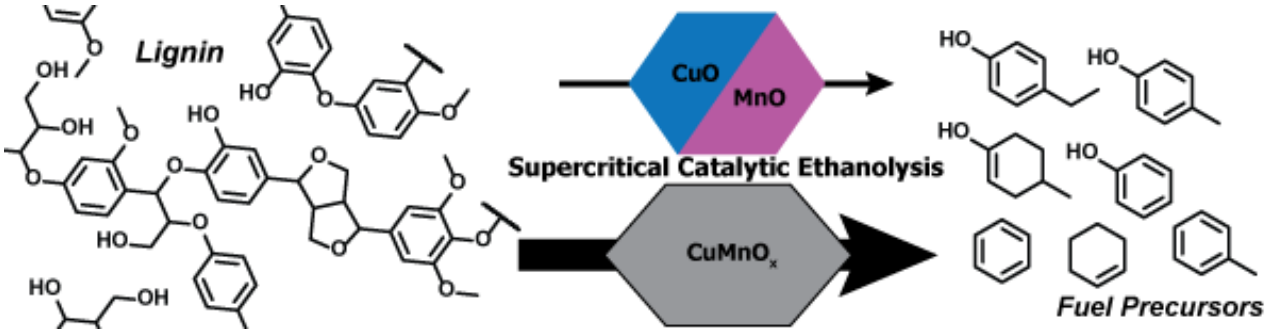


Copper Manganese Spinel Oxide for Enhanced Solvolysis of Technical Lignin

Davey F. de Waard[1], Panos D. Kouris[1], Michael D. Boot[1], and Emiel J.M. Hensen[1]
[1]*1Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands*

Keywords: Lignin, Catalytic solvolysis, Ethanolysis, Copper-Manganese, Spinel Oxides

The aromatic nature of lignin makes it a prime feedstock for the production of renewable aromatic compounds. Due to its recalcitrant and heterogenous nature, extraction of aromatic monomers has been proven challenging thus far.[1] The use of a Cu-Mg-Al mixed metal oxide can effectively depolymerise technical lignin in supercritical ethanol.[2] In an effort to improve the activity of such mixed oxides, various first row transition metals were screened as dopants for the Cu-Mg-Al mixed metal oxide. Among these, Mn showed promising performance in terms of monomer extraction and solvolysis performance. XRD and XPS indicated the formation of a Cu-Mn spinel oxide. Cu increased the reducibility of Mn, indicating its potential role in the observed synergy. In order to investigate the role of the Cu-Mn spinel oxide in the catalytic solvolysis in more detail, various spinel oxides were synthesized through impregnation and co-precipitation methods. Their catalytic performance was determined in the solvolysis of technical soda lignin (P1000) in supercritical ethanol. Proximity effects of the Cu and Mn species were evaluated using single metal oxide catalysts as reference. The Cu-Mn spinel oxide was found to produce the highest aromatic monomer yield of 35 wt% with full solvolysis of lignin oligomers.



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The supported Cu-Ni bimetallic catalysts for vapor phase conversion of furfuryl aldehyde

J. Kaim, M. Śliwa, K. Samson, M. Zimowska, M. Ruggiero-Mikołajczyk, J. Podobiński, M. Witko, D. Rutkowska-Zbik*

Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Krakow, Poland
**dorota.rutkowska-zbik@ikifp.edu.pl*

Keywords: furfuryl aldehyde, hydrogenation, decarbonylation, bimetallic catalysts

Introduction. Furfuryl aldehyde (furfural, FAL) is an aromatic compound, which is commonly known as an important platform molecule. It can be produced in huge quantity via acid hydrolysis of pentoses, five-carbon sugars, such as xylose and arabinose [1]. The catalytic conversion of FAL leads to the broad range of products, which are valuable intermediates from the point of view of the bio-fuels technology and chemical industry. The distribution of products strongly depends on the catalyst nature (metal type, support properties) and the reaction conditions. Among detected products, furfuryl alcohol (FOL) and 2-methylfuran (2-MF), are of great importance. The hydrogenation of FAL can be performed over catalysts containing transition metals: Cu, Ni, Co, Fe, Pt, Pd [2]. The goal of this work was to study the FAL conversion pathways over bimetallic Cu-Ni supported catalysts and influence of the support type on the catalyst final activity.

Experimental/methodology. The bimetallic Cu-Ni catalysts were supported on SiO_2, CeO_2 and ZrO_2 via wet impregnation method. The obtained catalysts, referred as $Cu_{1.0}Ni_{1.0}/ZrO_2$, $Cu_{1.0}Ni_{1.0}/CeO_2$, $Cu_{1.0}Ni_{1.0}/SiO_2$ and $Cu_{2.5}Ni_{2.5}/ZrO_2$, $Cu_{2.5}Ni_{2.5}/CeO_2$, $Cu_{2.5}Ni_{2.5}/SiO_2$, were characterized by the following several techniques: XRD, H_2-TPR, N_2-physisorption, XRF and SEM/EDS. The catalytic reaction was performed in the fixed-bed flow reactor. The products and substrates were analyzed using gas chromatograph equipped with FID detector. For typical measurement, the 150 mg of catalyst was mixed with quartz and placed in the reactor. Next, the sample was reduced in the mixture of 20%H_2/Ar and temperature was lowered to 120 ^oC. The thermostated bubbler at 54.5 ^oC was used to generate vapors of FAL. The volume ratio of FAL to hydrogen in the reaction stream was 1:10. The catalytic reaction was carried out at 120°C, 160°C and 200°C.

Results and discussion. The XRD analysis revealed the presence of CuO and NiO phase only in the case of catalysts supported on SiO_2. On the other hand, no XRD reflexes assigned to active phases are present in the diffraction patterns of catalysts supported on CeO_2 and ZrO_2. This can result from the very small crystallites of CuO and NiO which are formed on the surface of CeO_2, below the detection limits of XRD. Nevertheless, the presence of copper and nickel on the support was confirmed by XRF analysis, which showed that determined concertation values of both active phases closely corresponds with nominal values. In the H_2-TPR profiles of bimetallic catalysts overlapping signals of CuO and NiO reduction are present. The position of these signal depends on the used supports and for all catalysts is below the reduction temperature of standard CuO and NiO. In the case of all catalysts, the conversion of FAL increases with the temperature of the reaction, reaching 73% for $Cu_{1.0}Ni_{1.0}/CeO_2$ at 160 ^oC. The selectivity to FOL is the highest when reaction is performed at 120 ^oC (33% for $Cu_{2.5}Ni_{2.5}/SiO_2$). The increase of temperature causes that selectivity to FOL drops and furan starts to dominate among detected products. This proves that decarbonylation pathway is favored over hydrogenation of FAL. Additionally, 2-MF and propane was also detected which suggests that hydrogenolysis and ring opening reactions occur over synthesized catalyst too.

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"Catalytic valorization of sugarcane molasses to 5- hydroxymethylfurfural (HMF) in water"

K. Morawa Eblagon[1,2]*, J. L. Figueiredo[1,2], M. Fernando R. Pereira[1,2]

[1]*LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*
[2] *ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*
[*]*keblagon@fe.up.pt*

Keywords: biomass conversion, 5-hydroxymethylfurfural, dehydration, sugarcane molasses

Introduction. Technologies transforming renewable carbon sources such as agroindustrial residues into chemicals or liquid fuels are urgently needed to address the energy crisis and environmental issues linked with the extensive reliance on fossil fuels. Within this context, sugarcane molasses (SCM), a waste product from the sugar industry, can be transformed into a versatile biorefinery intermediate called 5-hydroxymethylfurfural (HMF) using a solid acid catalyst in water. The dehydration of SCM involves multiple steps, which can be catalysed by Lewis acids in combination with organic acids [1], or amorphous carbon with strong Brønsted acid sites [2].

Experimental/methodology. Environmentally friendly carbon catalysts derived from rice starch were obtained via a hydrothermal carbonization method. The catalysts included: i) amorphous carbon with only Brønsted acid (BA) sites in the form of -SO_3H groups (abbr. C-SO_3H) and ii) a bifunctional catalyst (abbr. C-P-SnO_2) having a combination of BA sites (i.e. P-OH groups) and Lewis acid (LA) sites (i.e. SnO_2). The conversion of sugarcane molasses to HMF was studied in water using a microwave reactor. In order to discard the influence of impurities present in industrial SCM, the reaction parameters were first optimized using synthetic SCM (i.e., a neat mixture of sucrose, glucose, and fructose) and then validated in industrial-grade SCM.

Results and discussion. HMF production from synthetic SCM was enhanced when high temperatures (190 °C) and moderate catalyst/substrate ratios (0.1) were employed in short reaction times (20-30 min). A higher HMF yield of 30.6% was obtained using C-SO_3H, containing only BA sites, compared to 25.9% recorded for bifunctional C-P-SnO_2. Insufficient isomerization of glucose to fructose was a major barrier to achieving higher yields of HMF from synthetic SCM using C-SO_3H. In contrast, LA sites on C-P-SnO_2 successfully catalysed glucose isomerization to fructose. However, the slower sugar to HMF conversion rate rendered a lower overall HMF yield on this catalyst.

When industrial-grade SCM was applied as a feedstock, a steep decrease in HMF yield from 30.6% to 12.5% was recorded using C-SO_3H. It was noted that the conversion of sugars (i.e., sucrose, glucose, and fructose) was higher in the case of crude feedstock. Still, the selectivity to HMF was significantly lower. The analysis of the reaction side-products showed that HMF was likely further converted to insoluble humin. The non-sugar impurities facilitated the side reactions in industrial SCM. Last but not least, different methods of industrial SCM pretreatment were considered to increase the yield of HMF.

Acknowledgments

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Designed seafood waste-biochar catalysts for sustainable biorefinery

Andreia F. Peixoto*, Inês S. Marques, Renata Matos, Marta Monteiro, Diana M. Fernandes

[1]*LAQV-REQUIMTE, Dep. de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto*
[*]*andreia.peixoto@fc.up.pt*

Keywords: biorefinery, biochar based catalysts, biomass conversion

Introduction. Despite the abundance of carbon in nature, a significant portion of the existing biomass carbon materials in livestock, agriculture, and marine fishery industry are currently being wasted. Most of seafood waste (SW) is disposed into landfills or back into the ocean being associated with several environmental issues. Because of the reactive amino-group, chitin-derivatives can serve as novel platform molecules for the synthesis of a plethora of industrially valuable chemicals and materials.[1,2] Following the concept of biorefinery and circular bioeconomy, the Shell4BioA project arise to meet these challenges targeting the production of biobased products including bioamines and designed biochar materials from SW aligned with green chemical principals and with the goals for the sustainable development. Several designed SW-biochar catalysts (sulfonic-acid functionalized and metal-supported) were prepared and used to produce biobased chemicals, biofuels and energy in a biorefinery concept.

Experimental/methodology. Shrimp shells obtained from portuguese marine fishery industry were frozen, dried, grounded (particle size < 0.5 mm) and stored in sealed bags at room temperature until use. Biochar-based catalysts were prepared according to modified procedures from literature[3,4]. Metals/metal oxides (Metal: Co, Fe, Co-Mo, Ni, etc.) were supported on the N-doped SW-biochar using co-precipitation, wet impregnation and ball milling mechanic impregnation.[3] The biochar-based catalysts functionalized with sulfonic acid groups were prepared by mechanical synthesis by mixing the biochar with the organic sulfonic acids precursors. All catalysts have been used in catalytic reactions for the production of biobased products: ethyl levulinate, furfuryl alcohol, methylfuran and bio-based amines.

Results and discussion. Herein, we present the preparation of several designed SW-biochars. The activation under chemical/physical experimental conditions allowed to obtain high surface areas (BET > 200 m^2/g).The sucessfully preparation of the funcionalized catalysts was verified by XPS, XRD, Raman, FTIR and SEM/EDS; the formation of highly porous structures was displayed in SEM and, XPS results showed the presence of N-functionalizations. Ethyl levulinate (EL) was obtained from 5-HMF with (EL yield = 90%) at 130 °C over the sulfonic acid funcionalized biochar (after 6 h reaction). The catalyst is recyclable without significant loss of catalytic activity. γ-Valerolactone (GVL) was also obtained (yield > 95 %) from furfural, as an additional valuable chemical and an intermediate in the production of fine chemicals using only water and formic acid at 280 ºC, 4h reaction using Co-Mo supported SW-biochar catalyst. All the catalytic results and the catalysts perfomance will be discussed according to the characterization results.

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Comparison of oxygen and hydrogen peroxide as oxidants for obtaining furoic acid from furfural over supported gold catalysts

P. Rapado, L. Faba, S. Ordóñez*

[1]*Department of Chemical and Environmental Engineering, University of Oviedo, Oviedo, Spain*
**sordonez@uniovi.es*

Keywords: furfural upgrading; sustainable polymers; aqueous-phase partial oxidation; biorefinery

Introduction.

Furfural is one of the most versatile bioplatform molecules since the technologies for its production from biomass are well-established and even commercially available. This fact is especially important in comparison to HMF, whose manufacturing procedures are less developed. Among the chemicals that can be synthesized from furfural, furoic acid (FCA) is of key relevance because of its chemical applications and, mainly, since its carboxylation produces the furfuryl dicarboxylic acid (a renewable monomer).[1] Two different oxidants are considered for FCA production from furfural, H_2O_2 (allowing working at mild temperatures and pressures) and air (cheaper and more sustainable, but requiring harsher reaction conditions). In both cases, gold catalysts are considered the most active ones.[2] The scope of this work is to compare both oxidations, identifying their key steps and proposing a comprehensive kinetic model.

Experimental/methodology.

The reactions were performed in a stainless-steel autoclave reactor of 0.5 L total volume of a 0.5 M solution of furfural. Experiments were carried out at 0.5 MPa of N_2 (H_2O_2) or in a pressure range of 0.5-2 MPa (pure O_2) comparing two catalysts: Au/TiO_2 and Au/Mg-Al (mixed oxides). Reaction products were analyzed by HPLC.

Results and discussion.

The high reactivity of H_2O_2 allows working at lower temperatures (50°C) than when using O_2 (no reaction observed below 80°C), but the selectivities to FA reached with H_2O_2 were markedly lower than those obtained with O_2. The optimum conditions with H_2O_2 lead to a FCA selectivity of 20 %, with a furfural conversion of 40 % (50°C, similar results for both catalysts). The selectivities to other by-products as maleic acid (MA) and 2-hydroxyfuran (HF) are in the same order of magnitude. The kinetic analysis of these data and those obtained with separate experiments with intermediate products suggest that both FCA and HF are primary products that undergo secondary reactions yielding MA, among other organic acids. The oligomerization of furfural to humins is not relevant at these conditions, likely because of the lower reaction temperature.

When using O_2 as the oxidant, the product distribution changes markedly, being possible to work at high conversions (>60%) with FCA as the only organic acid detected (Au/TiO_2, 100ºC, 0.2 MPa). At higher temperatures, the formation of MA starts to be relevant, but always at one order of magnitude lower than the FCA selectivity. By contrast, the formation of insoluble humins is more important working with O_2 (leading to carbon balance unclosures of about 20 %; <5 % with H_2O_2). Higher O_2 pressures have a positive effect on the FCA selectivity because of two concomitant causes, the increase in the FCA formation rate (more marked in the case of using Au/MgAl), and the unexpected inhibition of the humins formation. Obtained results were fit to a mechanistic kinetic model useful for both understanding the reaction mechanisms and designing the optimum chemical reactors for this purpose.

Acknowledgments

The authors aknowledge grant PID2020-112587RB-100, and BIOHYDROMER funded by AEI 10.13039/501100011033.

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Continuous-flow liquid-phase valorisation of furfural to γ-valerolactone over Ti/Zr/O catalysts

A. Allegri, A. Saotta, N. Dimitratos, G. Fornasari, S. Albonetti*

Department of Industrial Chemistry, Alma Mater Studiorum University of Bologna, Bologna, Italy
**Stefania.Albonetti@unibo.it*

Keywords: Furfural, γ-valerolactone, continuous flow, Ti/Zr/O catalysts

Introduction. The molecule γ-valerolactone (GVL) has recently gained great attention as a green solvent and additive as well as versatile building block for chemical synthesis [1]. Biomass-derived GVL is currently produced by a multistep process using acidic and metal-based catalysts and this strategy suffers from several limitation. GVL can also be produced by acid-catalysed cascade reactions from furfural (FU) using catalytic transfer hydrogenation (CTH) reaction as alternative to molecular H_2 reductions. This process can be industrially relevant due to the high availability of FU on industrial scale and his good solubility in most solvent, moreover the use of CTH approach, with alcohols acting as solvent and H-donor can maximize the product yields without the use of precious metals, high H_2 pressure and an excessive number of operations. The direct conversion of FU to GVL in a single reaction step requires the development of appropriate catalysts with both Lewis and Brønsted acidity. Zr-Al materials and zeolite were demonstrated to be active in the reaction in batch reaction,[2] nevertheless, considering the growing interest in FU conversion to GVL, the developing of more efficient and scalable process using CTH approach in continuous mode is still necessary.

In this study, we demonstrated the application of Ti/Zr/O as effective catalysts for the one-pot reaction of FU into GVL in a continuous flow liquid phase reactor using 2-propanol as solvent and H donor.

Experimental. Ti/Zr/O catalysts ad different Ti/Zr ratio were synthesized via coprecipitation in 5 M NH_4OH, then digested for 48h at pH 9 before calcination at 500°C. The materials were characterised through XRF, XRD, NH3-TPD and porosimetry. Catalytic tests were carried out feeding the solution of FU in 2-propanol (2-propanol/FU molar ratio 200) onto 1 mL of catalyst kept at 180°C, with residence time of 10 min.

Results and discussion. While XRD highlighted no noticeable segregation of either titania or zirconia in the synthesized materials, NH_3-TPD revealed a nonlinear effect of the increase of Ti content on the acidity of the catalysts: a maximum of acid sites density is registered with an equimolar amount of Ti and Zr. This was correlated with the catalytic performances, showing a maximum in GVL selectivity. The mechanism of the reaction has been studied by investigating the reactivity of the intermediates and varying reaction parameters, such as contact time and temperature. The long-time performance of the catalysts has been studied showing promising catalytic stability and the catalytic data have been correlated with the characterisation of the fresh and used catalysts.

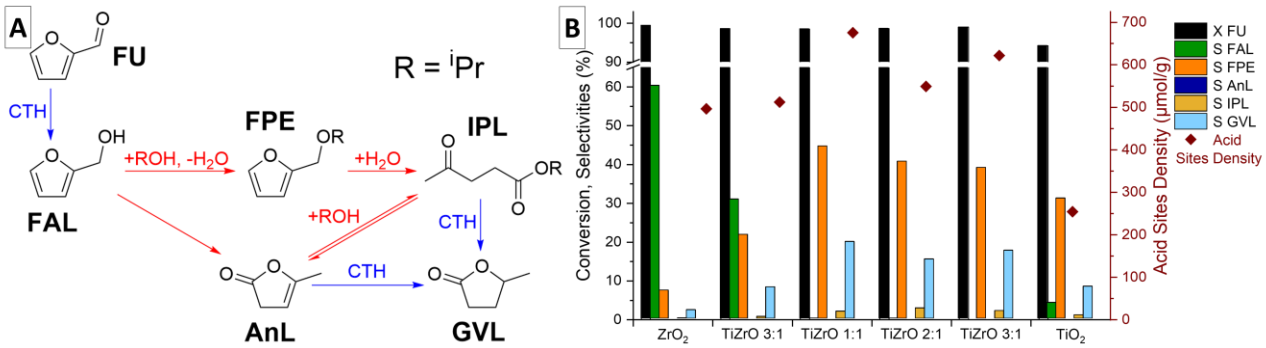

Figure 1. Scheme of the studied reaction (A). Catalytic performances of the tested materials (B).

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Selective C–O hydrogenolysis of terminal C–OH bond in 1,2-diols over rutile-titania-supported iridium-iron catalyst

B. Liu[1], Y. Nakagawa[1,2,*], C. Li[1], M. Yabushita[1,2], K. Tomishige[1,2,3,*]

[1]Department of Applied Chemistry, School of Engineering, Tohoku University, Sendai, Japan

[2]Research Center for Rare Metal and Green Innovation, Tohoku University, Sendai, Japan

[3]Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai, Japan

*yoshinao@erec.che.tohoku.ac.jp; tomishige@tohoku.ac.jp

Keywords: biomass-derived polyols, secondary alcohol, hydrodeoxygenation, regioselectivity

Introduction. Selective recognition and activation of target C–O bonds of substrates are critical but quite challenging for the transformation of renewable biomass-derived polyols to platform chemicals in the chemical industry. The C–O hydrogenolysis for the secondary OH groups to produce primary alcohols from 1,2-diols has been achieved so far by using Ir–ReO_x and Pt–WO_x catalysts.[1-2] In stark contrast, effective catalysts have not yet been developed for selectively removing the primary OH groups of biomass-derived polyols. In order to extend the scope of products from biomass, various types of catalysts with different regioselectivity in hydrogenolysis of polyols are necessary. The catalysts with good selectivity to secondary alcohols from 1,2-diols will offer a new route for biomass conversion, such as 2,3-butanediol (a platform chemical for pharmaceutical, cosmetic, and polymer industries) from erythritol. Here, Ir-MO_x/rutile TiO_2 (M: Fe, Mn, Co, Ni, Cu, Zn Ga, In, Sn) was explored for 1,2-butanediol (1,2-BuD) hydrogenolysis as a model reaction to develop catalyst with such regioselectivity, considering available biomass-based 1,2-BuD from erythritol[3] and wide applications of 2-BuOH (such as fuel additive and solvent). Ir-FeO_x/rutile was found to be effective for the removal of primary OH group of 1,2-diols and related alcohols by hydrogenolysis.[4]

Experimental. Ir-MO_x/rutile catalysts were prepared by a sequential impregnation method. The activity test was carried out in a stainless-steel autoclave (190 mL) equipped with an inner glass vessel. The organic substances in both liquid and gas phases were analyzed by FID-GC and HPLC.

Results and discussion. As shown in Figure 1, the selectivity to 2-butanol (2-BuOH) over Ir/rutile TiO_2 (Ir = 5 wt%) was moderate (53%) initially but rapidly decreased (39%) at longer reaction time (72 h). Addition of Fe to Ir/rutile enhanced both activity and selectivity, while other screening modifiers were not effective. Fe/Ir ratio was further optimized as 0.25. Other oxide supports including anatase TiO_2 gave lower selectivity to 2-BuOH. Severe deactivation phenomenon was observed during reuse experiment over the Ir-FeO_x/rutile (Ir = 5 wt%, Fe/Ir = 0.25) catalyst. Interestingly, the reusability of catalyst was reinforced by optimizing the preparation method (involving the calcination followed by reduction and subsequent loading of Fe; Ir_{c-r}-FeO_x/rutile). Ir_{c-r}-FeO_x/rutile (Ir = 5 wt%, Fe/Ir = 0.25) was reusable at least 4 times and gave high 2-BuOH yield (64%) from 1,2-BuD. Such regioselectivity given by Ir_{c-r}-FeO_x/rutile was also demonstrated in the hydrogenolysis of related alcohols (Figure 2): 1,2-propanediol to 2-propanol (yield: 53%), glycerol to 2-propanol (yield: 30%), 1,3-butanediol to 2-BuOH (yield: 83%), and erythritol to 2,3-butanediol (yield: 30%). The characterization with XRD, H_2-TPR, TEM-EDX, XANES, EXAFS, CO adsorption and DRIFT of adsorbed CO suggested that Ir particles with Ir-Fe alloy on the surface (3 nm) modified with FeO_x species were constructed on the active catalyst. The active sites should be the interface between Ir-Fe surface alloy and FeO_x species.

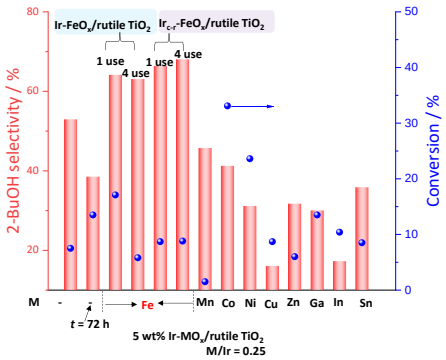

Figure 1. 1,2-BuD hydrogenolysis over Ir-MO_x/rutile catalysts.

Reaction conditions: 1,2-BuD = 0.5 g, H_2O = 4 g, m_{cat} = 0.2 g, $P(H_2)$ = 8 MPa, T = 453 K, t = 24 h.

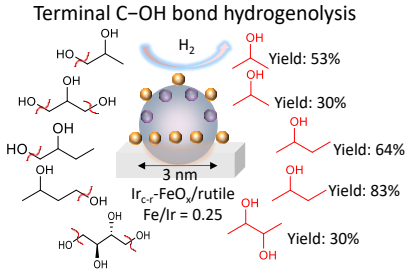

Figure 2. Related alcohols hydrogenolysis.

Acknowledgments

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Evaluation of anisole deoxygenation reaction pathway over nickel catalyst

Snehasis Dutta[1], Bogdan Shumeiko[1*], David Kubička[1, 2*]

[1]*Department of Petroleum Technology and Alternative Fuels, University of Chemistry and Technology, Technická 5, 166 28 Prague, Czech Republic*

[2]*Technopark Kralupy, Žižkova 7, 278 01 Kralupy nad Vltavou, Czech Republic*

*** shumeikb@vscht.cz, kubickad@vscht.cz

Keywords: Deoxygenation; Anisole; Nickel catalyst; Reaction pathway; Reaction equilibrium.

Introduction. Lignin is a major natural polymer that constitutes about 30 % of biomass and it is a potential source of sustainable chemicals. Depolymerization of lignin results in phenolics like guaiacol, syringol, and catechol. Deoxygenation (DO) of these compounds may produce aromatics (eg., benzene) from sustainable feedstock (waste lignocellulosic biomass). DO of lignin-derived phenolics also produces hydrocarbons with boiling points in the range of transportation fuels. In this study, anisole (methoxybenzene) was chosen as a model compound for the investigation of the DO pathway over nickel-based catalysts.

Experimental/methodology. 5-16 wt% Ni/Al_2O_3 catalysts were prepared by wet impregnation using nickel nitrate as the precursor and alumina granules as the support. The catalysts were characterized using ICP-OES, XRD, BET, TPR, and H_2-chemisorption. Testing of the catalysts for DO of anisole was carried out in a continuous flow reactor at 80-300 °C, 5-40 bar H_2, and weight-hourly space velocity (WHSV) 12-180 h^{-1}. The use of a wide range of reaction conditions allowed the depiction of the reaction progression and equilibrium conditions. The most abundant reaction intermediates like methoxycyclohexane and cyclohexanol were also deoxygenated to study the side reactions and trace intermediates.

Results and discussion. The DO of anisole initiates through hydrogenation of the aromatic ring, resulting in the formation of methoxycylohexane, at temperatures lower than 160 °C. At temperatures above 160 °C, methoxycyclohexane undergoes demethoxylation to cyclohexane. Traces of cyclohexanol (maximum selectivity of 6%) were detected, suggesting the demethylation of anisole throughout the observed temperature range. Phenol which is a precursory intermediate for cyclohexanol formation was seen only at very low anisole conversion at WHSV 120 and 180 h^{-1}, 270 °C, and 5 bar. At moderate pressures (5-12 bar), dehydrogenation of cyclohexane to benzene was observed above 220 °C. Deoxygenation experiments with methoxycylohexane and cyclohexanol (the most abundant reaction intermediates) showed the significance of hydrogenation-dehydrogenation reaction equilibrium in determining the anisole DO product distribution. Additionally, in the pressure range of 5-12 bar transmethylation reactions were observed above 260 °C. This work shows that the DO of anisole over nickel catalysts may result in a myriad of compounds depending on the process conditions.

Acknowledgments

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Beneficial Mo-W Synergy in Supported Catalysts for the HDO of m-cresol

Bertha Farah[1*], Carole Lamonier[1], Christine Lancelot[1], Pascal Blanchard[1], Frédéric Richard[2]

[1]*Unité de Catalyse et Chimie du Solide UCCS, University of Lille, C3 building, 59655, Villeneuve d'Ascq, France*

[2]*Institut de Chimie des Milieux et Matériaux de Poitiers IC2MP, University of Poitiers, B27 building, 86073, Poitiers, France*

[*]*bertha.farah@univ-lille.fr*

Introduction

Hydrodeoxygenation (HDO) is a hydrotreating catalytic process that is being widely investigated nowadays. Among its several applications, HDO can be used to transform O-rich liquids derived from biomass to high value aromatic hydrocarbons that are currently produced from depleting petroleum-derived chemical processes. Catalyst choice is essential in directing HDO reaction pathway and product selectivity. Molybdenum oxide catalysts showed high yields of aromatics production from phenolic compounds issued from biomass, which was attributed to the oxophilic character of Mo that favors the direct cleavage of the $C_{aromatic}$– O bond (DDO pathway) [1]. Nevertheless, MoO_3 catalysts were reported to be less active than sulfide ones in HDO [2]. It then seemed interesting to investigate how to obtain both activity and selectivity into aromatics enhancements. Adding W was considered due to an observed synergy with Mo in sulfide catalysts for HDS [3]. The better sulfidation of both elements suggested their easier reducibility that could be beneficial in HDO where Mo^{5+} species are suggested as active sites [1].

Methodology

Mixed MoW oxides catalysts having 10 wt.% total metal content supported on ZrO_2 were prepared from synthesized $H_4SiMo_xW_{12-x}O_{40}$ heteropolyacids with x = 0, 3, 6, 9 and 12 through dry impregnation. The catalysts were then characterized by several techniques (ICP, N_2-physisorption, XRD, Raman, H_2-TPR and XPS) and they were evaluated in the HDO of m-cresol at 340°C under 30 bar.

Results and discussion

Unlike Mo, W alone exhibited poor activity in these conditions. Nevertheless, a beneficial synergy was observed between W and Mo. In terms of activity, the rate constants of mixed MoW catalysts were found to be higher than the estimated values calculated from the experimental rate constants of $SiMo_{12}/ZrO_2$ and SiW_{12}/ZrO_2 (Figure 1), especially in the case of the most active catalyst $SiMo_9W_3/ZrO_2$. Furthermore, the selectivity to aromatic toluene improved in the presence of W, reaching almost 100%. It was concluded from XPS analysis that the presence of W improved Mo reducibility. A correlation was found between the quantity of Mo^{5+} atoms on the reduced catalysts and the catalytic activity, confirming that Mo^{5+} species can be considered as active sites for HDO. The increase in the amount of Mo^{5+} was obtained using mixed MoW precursors, mainly for $SiMo_9W_3/ZrO_2$.

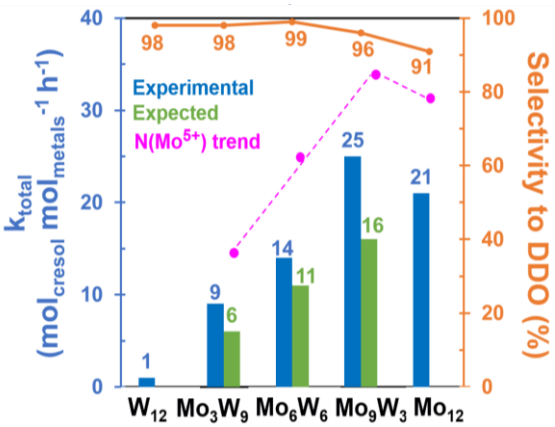

Figure 1 : Effect of W incorporation into Mo catalysts on activity, selectivity and reducibility

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Bio-glycerol hydrodeoxygenation to propylene: Optimizing the reaction conditions and exploring the reaction routes over Mo-based catalyst

G. Ioannidou[1], A.A. Lemonidou[1,2*]

[1]*Laboratory of Petrochemical Technology, Chemical Engineering Department, Aristotle University of Thessaloniki, University Campus, Thessaloniki 54124, Greece*

[2]*Chemical Process Engineering Research Institute (CERTH/CPERI), P.O. Box 60361 Thermi, Thessaloniki 57001, Greece*

[*]*alemonidou@cheng.auth.gr*

Keywords: Propylene, Molybdena catalysts, Hydrodeoxygenation, glycerol

Introduction.

The market demand for propylene as an important petrochemical intermediate continues to grow with a stable annual rate of 4%. With the majority of propylene being produced from fossil-based processes, the need for new sustainable routes is imperative [1]. An alternative way is by utilizing biomass and its derivatives, such as glycerol (a by-product from biodiesel process). Complete glycerol deoxygenation along with a formation of a C=C bond is a challenging path that could lead to propylene. This work refers to one-step glycerol hydrodeoxygenation (HDO) to propylene over molybdenum based catalysts, as it was found that they are attractive candidates for such reactions [2]. The effect of reaction parameters is exploited and optimized via response surface methodology.

Experimental/methodology.

Molybdenum based catalyst (8.7wt% Mo loading) supported on a commercially availabe black carbon (BC) Vulcan XC72 (Cabot) was prepared by wet impregnation method [2] and evaluated in a high-pressure fixed bed reactor (FlowCat, HEL), in vapor phase, using 10wt% aqueous glycerol solution. Prior to reaction, the catalyst was reduced ex-situ at 500°C for 30min. The X-ray diffractometry (XRD) technique, H_2 temperature program reduction (TPR) and X-ray Photoelectron Spectroscopy (XPS) were performed to determine the main physicochemical properties of the catalyst, while CH_3OH temperature programmed surface reaction (CH_3OH-TPRS) was applied to indentify the nature of the catalyst active sites.

Results and discussion.

The effect of reaction parameters (T:240-280°C, P^{o}_{H2}=8.7-61.5bar, P^{o}_{H2}/P^{o}_{glyc}=22-250, LHSV=0.4-1.2h^{-1}, W/F=211-422$g_{cat}/mol_{glyc}h$) was studied at constant TOS=4h. The parametric study indicated that increased temperature, hydrogen availability (P^{o}_{H2} and/or P^{o}_{H2}/P^{o}_{glyc}) and W/F are key parameters for propylene production. The main product detected in liquid phase is 1-propanol, in addition with the partially deoxygenated products, such as 2-propenol and propanal. The reaction was optimized using three response surface prediciton models expressing the effect of process parameters (P^{o}_{H2},P^{o}_{H2}/P^{o}_{glyc},LHSV,W/F) on responses (propylene yield and rate, sum yield of propanal and 1-propnol). Under optimum reaction conditions glycerol is completely converted to propylene achieving 71% yield at 60bar system pressure and 280°C. Furthermore, catalyst stability was investigated and the results showed that the catalyst remained stable for the first 10h, while lost only ~35% of its initial activity after TOS=30h. XPS confirmed the presence of the reduced Mo^{4+},Mo^{5+} species which are most likely the active sites of the reaction while CH_3OH-TPRS indicated that Mo^{4+},Mo^{5+} host redox/acid sites. The reaction pathway of glycerol to propylene was also examined by performing experiments with the main intermediate products formed. The results suggested that 2-propenol is selectively converted to propylene with the highest rate indicating that it is the primary intermediate of glycerol HDO over Mo/BC. 2-propenol isomerization to propanal is a secondrary route with the latter being converted to 1-propanol due to H_2 presence.

Acknowledgments

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Sulfided Ru/AC as a Prospective Catalyst for HDO in Supercritical Water

A. Kurlov[1*], D. Baudouin[1], F. Vogel[1,2]

[1] *Bioenergy and Catalysis Laboratory, PSI, Villigen, Switzerland;*
[2] *Institute for Biomass and Resource Efficiency, FHNW, Windisch, Switzerland.*
[*] *alexey.kurlov@psi.ch*

Keywords: Ruthenium-based catalyst, Deoxygenation, Black liquor, Sulfur, Supercritical water

Introduction. The Black Liquor to Fuel (BL2F) project, a EU Horizon 2020 project, aims to produce high quality marine and aviation fuels from pulp mill by-product, i.e. black liquor.[1] The first step of the process is the conversion of the black liquor *via* hydrothermal liquefaction (HTL) to intermediate HTL-oil.[2] A second key step is the development of integrated hydrothermal hydrodeoxygenation (iHDO) process in supercritical water (SCW) conditions. This step aims to remove part of the sulfur and oxygen from the HTL-oil and upgrade it to a more stable and easily transportable fuel intermediate. The operational conditions impose special demands on the catalyst of choice, i.e. the catalyst should be stable under continuous SCW flow and be sulfur tolerant. In this work, we will report the catalytic HDO of isoeugenol, as a model compound for HTL-oil, over metallic and sulfided Ru/AC (Ru nanoparticles supported on activated carbon) catalyst.

Experimental/methodology. A Ru/AC catalyst was provided by Ranido (Prague, Czech Republic). Ru-S/AC, a sulfided catalyst, was prepared in a batch reactor under H_2 atmosphere in a mixture of hexane and dimethyl disulfide (DMDS) at 350 °C for 4 h. The HDO experiments were performed with isoeugenol as a model compound. Isopropanol was used both as a solvent and as an *in situ* H_2 source during the reaction. The catalytic activity was assessed in a continuous flow fixed-bed reactor operated at 400-410 °C and 30 MPa using 35 % isopropanol and 5 % isoeugenol/ 35 % isopropanol in water (vol.%) solutions with a controlled space velocity (WHSV = 425 − 8500 $g_{Org}\ g_{Ru}^{-1}\ h^{-1}$). The gaseous products were analyzed online with a micro-GC. The liquid products were analyzed with GC-FID and GC-MS.

Results and discussion. The catalyst performance was assessed under SCW conditions in a continuous flow. Though Ru/AC was found to be highly active for supercritical water gasification (SCWG) of isopropanol, the gasification rate was found to be strongly inhibited when isoeugenol was added to the feed. Micro-GC analysis showed a gas composition typical for SCWG, i.e. a mixture of CH_4 and CO_2 with ca. 10 % of H_2, indicating a sustainable *in situ* H_2 production in the reactor. The GC-FID analysis of the liquid products revealed a complete conversion of isoeugenol with WHSV strongly influencing the product composition. Specifically, while dihydroeugenol was the main product at a high space velocity, the reduction of WHSV shifted the reaction towards phenolic compounds with 4-propylphenol being the main product.

Next, the HDO activity of preliminary sulfided Ru/AC catalysts was assessed. Ru-S/AC was found to be rather inactive for SCWG. That may be explained by the sulfur poisoning of Ru being one of the main deactivation mechanisms in SCWG.[3] However, a significant amount of H_2 was produced *via* dehydrogenation of isopropanol to acetone. The GC-FID analysis of the liquid products revealed a complete conversion of isoeugenol to a variety of compounds. A moderate amount of propylbenzene and propylcyclohexane was detected among them indicating a complete deoxygenation of isoeugenol over sulfided Ru-S/AC catalyst. Overall, those results demonstrate that sulfided Ru/AC can be a promising catalyst for the HDO of S-rich HTL-oil under SCW conditions.

Acknowledgments
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We kindly acknowledge Ranido s.r.o. (Prague, Czech Republic) for providing the Ru-based catalyst.

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Crystal phase effects on the structure and performance of Nickle nanoparticles for H_2-free glycerol conversion to alanine

Jiachen Li, Paolo P. Pescarmona*

Chemical Engineering Group, Engineering and Technology institute Groningen (ENTEG), University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.
**Corresponding Author's E-mail address: p.p.pescarmona@rug.nl*

Amino acids are important components of proteins, which are produced mainly by fermentation. There is growing interest in developing altervative and sustainable methods for producing amino acids, particularly alternative the approaches that use biobased feedstock [1] [2] [3]. For instance, the use of glycerol derived from biomass to produce alanine repsents one of the environmentally friendly process to obtain amino acids[2]. Theoretically, the process involves two steps: (*I*) catalytic dehydrogenative oxidation of glycerol to lactic acid; (*II*) convertion of lactic acid to alanine via amination (as shown in Figure 1). The reaction is typically performed in a hydrogen atmosphere using costly noble metal catalysts[1] [2] [3].

In this work, we prove that it is possible to synthesize alanine by the reaction of glycerol and NH_3 without additional H_2 and employing a non-noble Ni-based catalyst. The results show that the catalytic performance of Ni/TiO_2 for step *II*, which is the rate-determing step, is largely controlled by the structure of TiO_2 (TiO_2-rutile v.s TiO_2-anatase). Ni/TiO_2-Anatase is unable to catalyse the conversion of lactate to alanine, while Ni/TiO_2-Rutile works effectively, resulting in a 53% alanine yield and a 72% lactate conversion (shown in Figure 1). Remarkably, the use of P25, a type of TiO_2 containing 20% TiO_2-rutile and 80% TiO_2-anatase, as the catalyst support for Ni/TiO_2 allowed to obtain nearly the same alanine yield (45%) as with Ni/TiO_2-rutile. While, a physical mixture of Ni/TiO_2-rutile (20 wt %) and Ni/TiO_2-anatase (80 wt %) catalysts led to a significanly lower lactate conversion and alanine yield. We propose that Ni nanoparticles on the rutile phase or at the interface between rutile and anatase are the active species in catalysing lactate amination as well as the whole process from glycerol to alanine.

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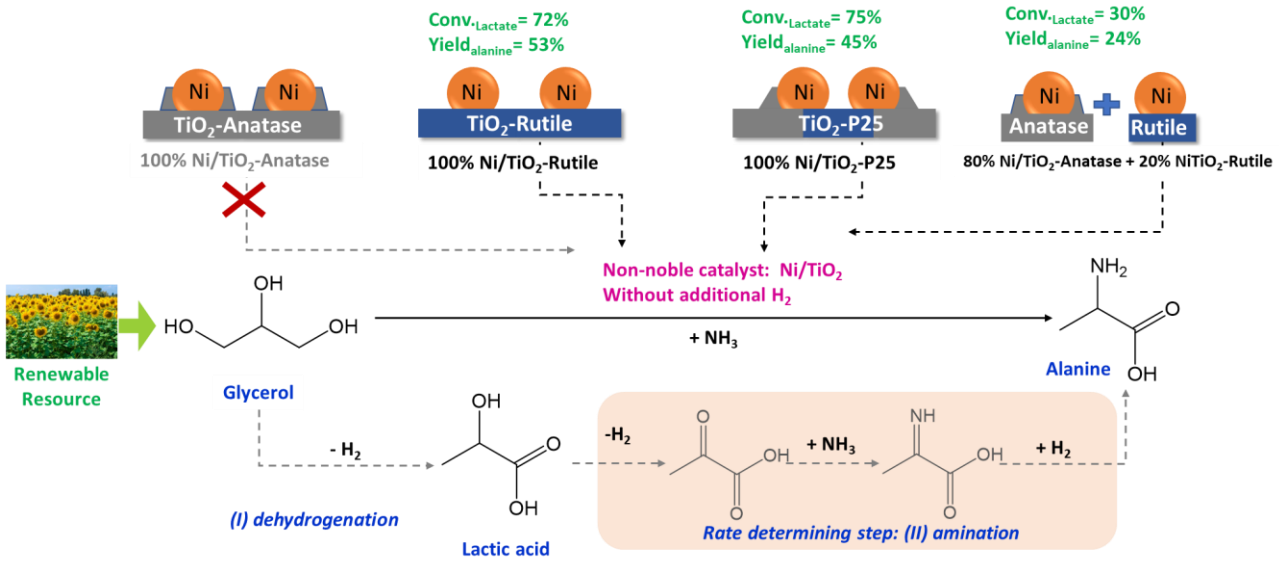

Figure 1. Graphical abstract

Catalytic Upgrading of Bioethanol to Ethylene over Various Hierarchical Zeolite Frameworks and Zeolites@LDHs Composites: From Laboratory-Scale to Pilot-Scale

C. Wattanakit*, C. Rodaum, P. Iadrat, A. Thivasasith, M. Ketkaew, P. Pornsetmetakul, P. Chaipornchalerm, W. Nunthakitgoson, S. Tantisriyanurak, A. Prasertsab

School of Energy Science and Engineering and School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong 21210, Thailand
**Corresponding Author's E-mail address: chularat.w@vistec.ac.th*

Introduction. The development of biorefinery is of crucial importance for academic and industrial perspectives. For example, bioethanol is one of the promising renewable resources, which can be converted to several chemical compounds, such as ethylene, diethyl ether, and acetic acid. In this context, various hierarchical zeolites have been successfully synthesized including ZSM-5, and FER[1-4], which can be applied as catalysts for greatly improved catalytic performances in bioethanol to ethylene. To gain insights into the mechanistic perspectives of bioethanol conversion, we also studied the effect of different zeolite frameworks on the catalytic transformation of bioethanol via *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)[2]. To further develop a catalyst for industrial use, the rational design of binder-free hierarchical zeolite monoliths derived from zeolite@layered double hydroxides (LDH) composites via extrusion and 3D printing technologies has been illustrated and they exhibit exceptional catalytic performances in bioethanol dehydration, eventually boosting ethylene yield up to 96%[1]. To tackle the industrial challenges, we also illustrated the application of the designer catalysts in the bioethanol dehydration to ethylene on a pilot-plant scale. This example provides a new perspective idea of using hierarchical zeolites and their composites in industrial bioethanol upgrading.

Experimental/methodology. Various hierarchical zeolite frameworks including ZSM-5 and FER were synthesized via a hydrothermal process. Subsequently, the binder-free extruded hierarchical zeolites were prepared by the transformation of zeolites@LDHs composites without using a commercial binder. The catalytic performance in bioethanol dehydration was studied using both lab-scale and pilot-scale fixed-bed reactors.

Results and discussion. Herein, we reported that the synthesized hierarchical zeolites with different frameworks enable bioethanol conversion in different mechanistic pathways. For example, the FER is highly selective to ethylene and inhibits the formation of by-products, showing a high ethylene yield (~95%). To further illustrate their applications in practical applications, the rational design of extruded hierarchical ZSM-5 monolith derived from zeolite@LDH composites has been illustrated via extrusion and 3D printing technologies. The designer catalyst applied in bioethanol dehydration boosts ethylene yield by over 93.4±2.2% (Figure 1).

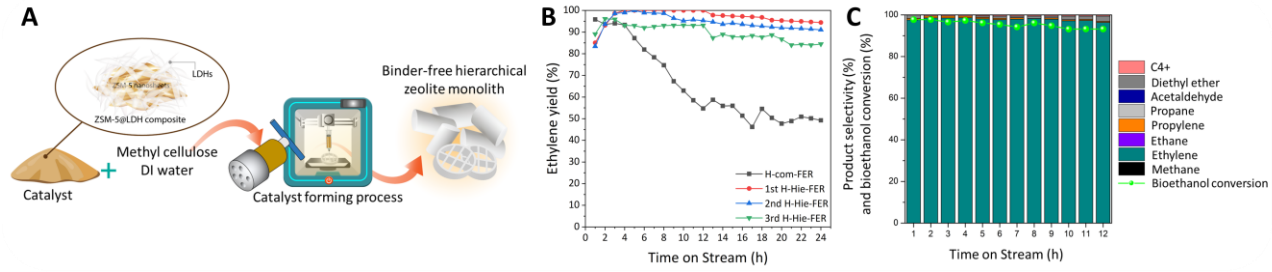

Figure 1. (A) Illustration of the fabrication of binder-free hierarchical zeolite monoliths[1] and (B-C) Catalytic performances in ethanol dehydration over different catalysts; (B) Hierarchical FER vs. Commercial FER[2]; (C) Binder-free extruded hierarchical ZSM-5[1].

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Unravelling the mechanism of selective oxidation of biomass-derived model compounds using TiO_2/g-C_3N_4/CdS heterojunction photocatalyst

D. Aboagye*, R. Djellabi, F. Medina, S. Contreras

Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans, 26, 43007 Tarragona, Spain

*dominic.aboagye@urv.cat

Introduction

Lignin remains the highest source of aromatic-based platform chemicals with a high potential to substitute fossil-based sources. However, the development of environmentally friendly and energy-saving approaches for its selective depolymerization remains a daunting task. Photocatalysis looks promising to harvest aromatic building blocks from lignin [1]. A critical challenge with photocatalysis is the development of highly selective photocatalysts for the transformation of aromatic-rich lignin under environmentally benign conditions [2,3]. Therefore, this study aimed to enhance the photo-responsiveness and intrinsic properties of the commercially available TiO_2 photocatalyst by co-incorporating CdS and g-C_3N_4 for lignin valorization.

Experimental/methodology

Herein, a ternary TiO_2/g-C_3N_4/CdS catalyst was synthesized via a sequential ball milling (Fritsch, Pulverisette P7 with 80 mL jar and milling balls of 10 mm diameter) and ultrasonication strategy. The photoactivity of the as-prepared photocatalyst was compared with other pure photocatalysts (g-C_3N_4, TiO_2, CdS) and binary catalysts (TiO_2/g-C_3N_4 and g-C_3N_4/CdS) by monitoring the conversion, selectivity, and yield of phenolic monomers from biomass-derived lignin model compounds (benzyl alcohol and 2-phenoxy-1-phenylethanol). For the photocatalysis experiments, the effect of catalyst loading (0.625, 1.25, and 1.875 g/L), reactions time (0,1, 3, 6, 9, 12 and 18 hours), and reaction media (water only, acetonitrile only and H_2O: acetonitrile) were investigated in a SUNTEST CPS+ solar simulator. The liquid fraction was analyzed by GC/MS to identify the products and quantification was done using an HPLC with a reverse phase C18 column. Mechanistic investigations were accomplished using radical quenching experiments using t-BuOH, $K_2S_2O_8$, p-benzoquinone, and $(NH_4)_2C_2O_4$ as •OH, electrons, O_2•− and photogenerated holes scavengers, respectively. The as-prepared catalysts were characterized using XRD, XPS, FTIR, TEM, and morphological analysis, while the optical properties were studied by UV–vis diffuse reflectance spectra analysis.

Results and Discussion

The ternary composite TiO_2/g-C_3N_4/CdS photocatalyst was highly selective towards the activation and cleavage of bonds in benzyl alcohol and 2-phenoxy-1-phenyl ethanol as compared to control photocatalysts. Meanwhile, the mechanistic investigation revealed that multiple radical species triggered the activation and cleavage of bonds in the model dimer, with holes being the most active species. This study will throw more strategies to enhance the photo-responsiveness of TiO_2 photocatalyst, and provide an understanding of the interaction between catalyst surface and complex lignin structures while providing novel routes for valorizing lignin to value-added platform chemicals via photocatalysis.

Acknowledgments

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Supported bimetallic (Ni/Cu) nanoparticles catalysts for the thermal hydrogenolysis of lignin model compounds

R. Abolivier[1*], J. A. Sullivan[1]

[1]*School of Chemistry, University College Dublin, Dublin, Ireland*
[*]*raphael.abolivier@ucdconnect.ie*

Keywords: Lignin, biomass valorization, heterogeneous catalysis, transition metals

Introduction.
Because of CO_2 release at end-of-life, the use of renewable resources for the generation of platform compounds (through biorefining processes) has recently attracted increased attention. Lignin is expected to become an important source of aromatic compounds. However, a viable lignin valorization technology remains to be developed. This project focuses on the development of sustainable (*e.g.,* using abundant transition metals) catalysts for ether bond hydrogenolysis of lignin model compounds.

Experimental/methodology.
Catalytic hydrogenolysis of a range of model compounds, each containing representative intramolecular lignin linkages, was investigated over different sets of ZSM-5 supported bimetallic (Ni/Cu) catalysts. A hydrothermal method was used to deposit metal-oxide nanoparticles on ZSM-5 and these nanoparticles were then reduced in a 3 % H_2/Ar atmosphere (at 500 °C) to prepare the catalysts.

Catalysts with different Ni/Cu ratios (1:1; 1:5 and 5:1) and different reduction temperatures (300 °C; 400 °C and 500 °C) were prepared. The catalysts were characterized using XRD, SEM/TEM, TGA-DSC and N_2 adsorption and the reactivity at elevated temperatures (up to 350 °C) in a H_2 pressurized (up to 80 bar) Parr reactor analyzed.

Results and discussion.

The deposition of dispersed nanoparticles on the ZSM-5 support was confirmed by electron microscopy and XRD. The catalysts were stable in the temperature range of interest (up to 500 °C) and maintained the high specific surface area of the zeolitic support (290-390 m^2/g)

The Ni/Cu ratio was identified as a key parameter for efficiency in the reaction. High conversions of benzyl phenyl ether (> 99.0 %) were obtained over a 1:1 ratio catalyst (with 5 wt% of each metal) after a 1 h reaction at 300 °C. However, under the same reaction conditions, over a catalyst with a lower metal loading (1 wt% each of Ni/Cu), a significantly lower conversion of the subtrate was obtained (~ 23 %). Investigation of catalysts with other Ni/Cu ratios suggested that the nickel surface was the active site for hydrogenolysis. A 5:1 Ni/Cu ratio led to a ~ 62 % conversion of benzyl phenyl ether whilst a 1:5 ratio did not lead to similar conversion to the 1:1 (1 wt%) material (~22 %).

Metal particle size effects on reactivity were investigated using catalysts prepared following different reduction temperatures (higher reduction temperature promoting particle sintering). Over a catalyst reduced at 300 °C, a low substrate conversion (~37 %) was obtained. A reduction of the nanoparticles at 500 °C led to a lower conversion of the model compound (~69 %) than a 400 °C temperature (> 99 %).

An investigation of the hydrogenolysis reaction using other model substrates (2-phenoxyacetophenone; 2-phenoxyacetophenol and diphenyl ether) was also undertaken. The reaction steps involved in 2-phenoxyacetophenone conversion to ethylbenzene, and phenol were elucidated. The role the C_α substituent (-OH; =O or -H) in β-O-4 model compounds was found be a key parameter for the catalyst's reactivity in the hydrogenolysis reaction.

Acknowledgments
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Catalytic Upgrading of Bio-Based 5-hydroxymethylfurfural to bio-based chemicals

A Achour[a*], H Ojagh[b], H P Ho[a], D Creaser[a], J Holmberg[b], O Pajalic[b], and L Olsson[a*]
[a] Competence Center for Catalysis, Chemical Engineering, Chalmers University of Technology, SE 412 96 Gothenburg, Sweden. [b] Perstorp AB, Industriparken, 284 80 Perstorp, Sweden.
*Corresponding authors: abdenour.achour@chalmers.se, louise.olsson@chalmers.se

Introduction. Biomass has emerged as a leading candidate feedstock for the chemical industry due to its renewable nature and the vast number of compounds it can be used to generate, many of which have similar or improved properties compared to their petroleum-based counterparts. The efficient production of biomass-derived chemicals is of technological importance for the transition to a more sustainable future. In this regard, 5-hydroxymethylfurfural (5-HMF) has been identified as a key platform chemical for the production of high value chemicals. Importantly, given the multi-functionalities of 5-HMF, the major difficulty to produce promising monomers is how to selectively hydro-convert a particular functional group(s) under mild-conditions. HMF could be hydrogenated to useful chemicals with applications as solvents, monomers, or precursors for the production of other high-value chemicals. In this project, two important monomers were primarily targeted, including 2.5-Bis (hydroxymethyl)furan (BHMF) and 2,5-Bis-(hydroxylmethyl) tetrahydrofuran (THFDM).

Keywords: Biomass, hydrogenation, HMF, Ni-based catalysts, heterogeneous catalyst.

Experimental. The experiments were carried out in a 300 mL stainless-steel Büchiglas reactor. In a typical experiment, a suitable amount of reactant, catalyst, and solvent were loaded into the reactor. The reactor was sealed and purged with hydrogen to remove the air at room temperature. The stirrer was started while heating with a stirring speed of 700 rpm. After the reaction, the reactor was cooled to room temperature and the liquid reaction mixture was thereafter collected. The catalysts and liquid products were separated for further analysis. Note that liquid samplings were taken for each experiment, first after 30 min and then every 1 h.

Results and discussion.
Initially, hydroconversion of 5-HMF to BHMF was studied over mono- and bimetallic supported catalysts in a batch reactor (Figure 1). We found that monometallic Ni/SiO_2 catalysts exhibited superior performance with a total yield of BHMF of up to 99 wt.% at 180 ºC, 75 bar H_2 for 2 h . This excellent performance might be attributed to the high Ni dispersion and low acidity of the support. The influence of Dimethyl sulfoxide (DMSO) contamination of HMF was also investigated due to the route used for its production (not shown for brevity). It was found that the conversion of HMF decreased by nearly 57% when an additional 8.5 wt% of DMSO was added to the reaction mixture [1]. Unlike BHMF, the production of THFDM requires hydrogenation of the furan ring. A good performance with complete conversion of BHMF, along with the highest selectivity of over 95% to THFDM, was attributed to the well-balanced properties of the support ZrO_2–SiO_2 (Figure 2)[2].

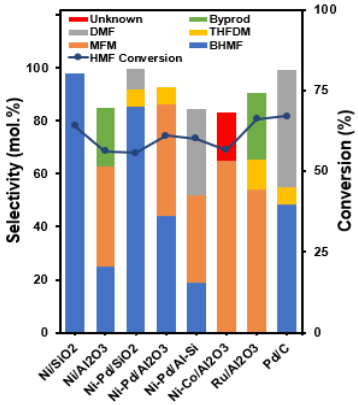

Figure 1. HMF conversion and products selectivity over various catalysts at 130 C, 40 bar, 6 h.

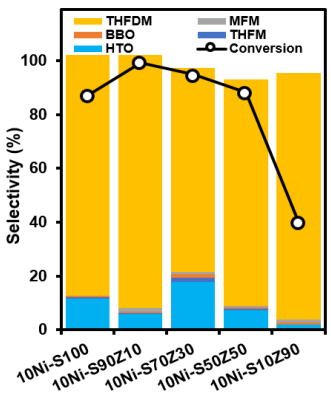

Figure 2. Effect of support on BHMF conversion and selectivity over 120 min

Acknowledgments. This work is a collaboration between Chemical Engineering Chalmers and Perstorp AB. We gratefully acknowledge the financial support from BioInnovation (2017–02702). We also acknowledge the financial support from the Centre for Chemical Process Engineering at Chalmers. We would also like to acknowledge the use of Chalmers Material Characterization Lab.

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Biomass/Plastic Catalytic Co-hydropyrolysis: Influence of Ni supported over C-Al_2O_3 derived from MIL-53 (Al)

C. A. Romero-Unda[1], K. J. Fernández-Andrade[1], S. Alejandro-Martín[1*]

[2]*Laboratory of Gas Chromatography and Analytical Pyrolysis (LGCAP), Univ. de Bío-Bío, Concepción, Chile*
[*]*Corresponding Author's E-mail address: salejandro@ubiobio.cl*

Keywords: Biomass and Plastics valorisation, Value-added chemicals, Py-GC/MS, MOF-Derived Materials.

Introduction. Catalytic co-hydropyrolysis might be a potential thermochemical process for producing value-added compounds, valorising plastics, and biomass residues. Catalysts derived from metal-organic frameworks could enhance selectivity toward aromatics compounds due to highly dispersed metal nodes on the surface, favouring hydrogenation reactions. This study evaluated the effect of nickel supported on carbo-alumina (Ni/C-Al_2O_3) on the selectivity of aromatics compounds (Benzene, Toluene, and Xylene) produced by biomass/plastic co-hydropyrolysis.

Experimental/methodology. MIL-53(Al) was heated up to 800°C to produce carbo-alumina (C-Al_2O_3) support and then impregnated with 15%Ni by incipient humidity. XRD, TPD-NH_3, and N_2-physisorption were used to characterise the catalysts. The co-hydropyrolysis assays were performed at 550°C/150 PSI H_2 on a Py-GC/MS (CDS5200 -Clarus689/SQ-8T) system, combining Oak wood, HDPE, and LDPE.

Results and Discussion. Amorphous C-Al_2O_3 formation and supported Ni nanoparticles (8.6 nm) were confirmed by XRD patterns. Due to the structural breakdown, the C-Al_2O_3 poses a lower surface area and larger pore size than its precursor (Table 1). However, Ni impregnation on C-Al_2O_3 had no significant effect on textural properties. Thus, Ni/C-Al_2O_3 was effective in hydrodeoxygenation reactions, reducing oxygenated compounds (OCs). Figure 1A shows a minimal production of OCs (1%) at higher heating rates and lower contact time for gases, minimising by-product reactions. At a lower heating rate (Figure 1B), the selectivity to hydrocarbons increased (72%), as well as OCs, due to further reactions [1]. Aromatic hydrocarbons resulted from Diels-Alders reactions between furans and olefins [2] and phenols hydrodeoxygenation [3]. Hydrogen was activated by supported Ni, while larger molecules were cracked on C-Al_2O_3 acidic sites [2,3].

Table 1. Textural properties of catalysts.

Catalyst	S_{BET} (m^2g^{-1})	V_{ADS} (cm^3g^{-1})	V_{DES} (cm^3g^{-1})	Pore size (nm)
MIL-53	698	0.15	0.13	4.9
C-Al_2O_3	272	0.26	0.22	13.3
Ni/C-Al_2O_3	216	0.29	0.26	7.0

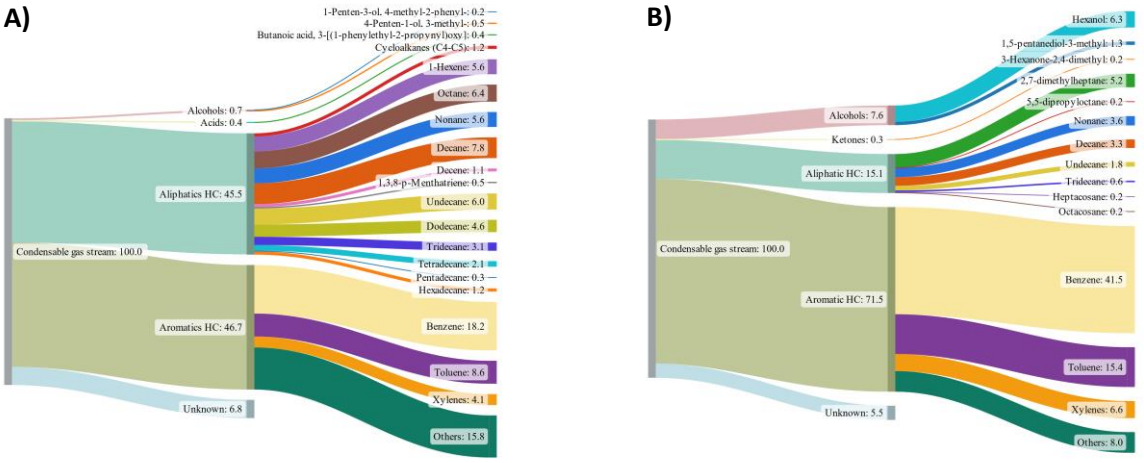

Figure 1. Product distribution using 87% Ni/C-Al_2O_3. A) LDPE, 10000°C/s. and B) LDPE, 12.5°C/s.

Acknowledgements. *The authors are grateful for support from Grant Number EQM 170077 and Grant Number 2160341 IF/R, UBB.*

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Multifunctional heterogenous catalysts for HMF hydrogenation.

B. Amin[1], J. Aubrecht[1], Andrey Smirnov[2] and D. Kubička[1,2]

[1] University of Chemistry and Technology Prague, Department of Petroleum Technology and Alternative Fuels Technická 5, Prague 6, 166 28, Czech Republic

[2]Technopark Kralupy, Náměstí Georga Karse 7/2, 278 01 Kralupy nad Vltavou, Czech Republic

Key words: 5-Hydroxymethyl furfural, Ru-TiO_2, SBA-15, hydrogenation

Introduction: Biomass is a plentiful renewable feedstock that has a huge potential to meet the challenges of sustainable and green chemistry. Lignocellulose is the main component of biomass, which can be converted into platform chemicals. Among them, 5-hydroxymethylfurfural (HMF) is called the sleeping giant, because of having 3 different functional groups (-OH, C=O and furan ring) whose potential remains underused. HMF can be reduced to various chemicals like 2,5-dimethylfuran, levulinic acid, and γ-valerolactone. However, it is challenging to reduce HMF into non-deoxygenated alcohols like bis-hydroxymethylfuran (BHMF) and bis-hydroxymethyltetrahydrofuran (BHMTHF) because of the selectivity issues. This research is conducted to design catalysts which can selectively reduce the aldehyde group of HMF only. For that reason, we designed a series of Ru-based catalysts.

Methodology: In this research, we impregnated 1 wt.% of Ru on different TiO_2-based supports (TiO_2/SBA-15, anatase, rutile, P25). TiO_2/SBA-15 was obtained by deposition of TiO_2 monolayer on SBA-15. All synthesized catalysts were in-situ reduced and tested in HMF hydrogenation. Catalytic tests were carried out in an autoclave at 220 °C and 70 bar H_2 pressure, using 1,4-dioxane as a solvent. After HMF reduction, liquid reaction product mixtures were analyzed by GC-FID to identify and quantify the individual reaction products. Structural, textural and composition properties of supports and Ru-containing catalysts were determined by XRD, TPR, BET and XRF.

Results: The reduction patterns obtained during TPR preliminary suggest different interactions of Ru with the different types of TiO_2 supports. When tested for HMF hydrogenation in a batch reactor for 3 h, the performance of the catalysts in terms of HMF conversion and desired products selectivity may be ranked in the following order Ru/Rutile>Ru/Anatase>Ru/TiO_2-SBA-15>Ru/high surface TiO_2. The selectivity of the desired product, BHMF, was 55 % and 30 % with Ru/Rutile and Ru/P25 catalyst, respectively. This work allows a better understanding of different metal-support interactions in selective hydrogenation of HMF.

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Ru/C Solid Foam Catalysts for Production of Sugar Alcohols: From Catalyst Development to Kinetic Modelling

G. Araujo-Barahona[1,2*], A. Goicoechea-Torres[1,2], K. Eränen[1], G. García-Serna[2], D. Murzin[1], T. Salmi[1]

[1]*Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Johan Gadolin Process Chemistry Centre (PCC), Åbo Akademi University, FI-20500 Turku/Åbo, Finland*
[2] *Grupo de Tecnologías a Presión (PressTech), Instituto de Bioeconomía de la Universidad de Valladolid (BioEcoUVa), Departamento de Ingeniería Química y Tecnologías del Medio Ambiente, Escuela de Ingenierías Industriales, Universidad de Valladolid, 47011 Valladolid, Spain*
**german.araujobarahona@abo.fi*

Keywords: hydrogenation, sugar alcohols, sweeteners, structured catalyst, biorefinery

Introduction. The use of structured catalysts, such as solid foams, represents a promising technology for the continuous production of high-value compounds derived from biomass such as sugar alcohols (e.g., sorbitol, xylitol, arabitol, galactitol). Solid foams combine the benefits of slurry and shaped body catalysts, i.e., thin catalyst layers that ensure high effectiveness factors, as well as open structures that minimize the pressure drop [1,2]. Sugar alcohols are generally produced by the catalytic hydrogenation of monomeric and dimeric sugars using a finely dispersed nickel-based catalyst in semi-batch reactors[3]. Even though this is a well-established industrial practice, process intensification is necessary to achieve production levels that allow biomass-derived resources to be utilized more efficiently. Therefore, the goal of this work was to develop a Ru/C foam catalyst and to study its catalytic activity and the hydrogenation kinetics of sugars and sugar mixtures at different temperatures, hydrogen pressures, and initial concentrations.

Experimental/methodology. Cylindrical pieces were cut from a commercially available aluminium foam sheet (96% porosity) and the pieces were coated via controlled polymerization of furfuryl alcohol mixed with poly(ethylene glycol) (M=8kDa) as pore-former. The coated foams were pyrolyzed, activated with air at 380°C, and acid-treated. Ruthenium incorporation was carried out through incipient wetness impregnation using ruthenium nitrosyl nitrate as the precursor, followed by *ex-situ* reduction at 300°C with hydrogen. The prepared Ru/C catalyst was used in experiments with xylose, arabinose, galactose, as well as binary sugar mixtures at 60-120°C and 20-60 bar hydrogen pressure. Finally, mathematical models based on plausible surface reaction mechanisms, i.e., non-competitive and semi-competitive adsorption between the carbohydrates molecules and hydrogen were developed to describe the experimental data.

Results and discussion. The carbon coating based on the formation and pyrolysis of poly(furfuryl alcohol) was identified as a critical step for the catalyst performance. In that sense, poly(ethylene glycol) (PEG) was added in the coating process to tune the porosity of the resulting carbon. The addition of 5 wt. % PEG resulted in a carbon with a ratio of meso-to-micropores volume of 1. The induced mesoporosity yielded a superior dispersion of the Ru nanoparticles (i.e., higher hydrogenation activity) and higher stability due to the spatial restriction induced by the mesopores. The obtained Ru loading on the catalyst was of 1 wt.% with an average nanoparticle size of 3 nm, which maintained a stable activity for more than 200 hours. Selectivities towards sugar alcohols exceeding 98% and sugar conversions reaching 50-99%, depending on the temperature, were obtained. The kinetic models based on non-competitive and semi-competitive adsorption of the sugars and hydrogen gave an excellent description of the concentration profiles and the impact of the process parameters along with insights on the complex mode of adsorption of sugars on the active sites of the catalyst.

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On the role of Pt oxidation state in the electrocatalytic dehydrogenation and oxidation of glucose

Matthijs van der Ham [1,2], Ellis van Keulen [1], Marc Koper [2], Akbar Asadi Tashvigh [1], Harry Bitter [1]*

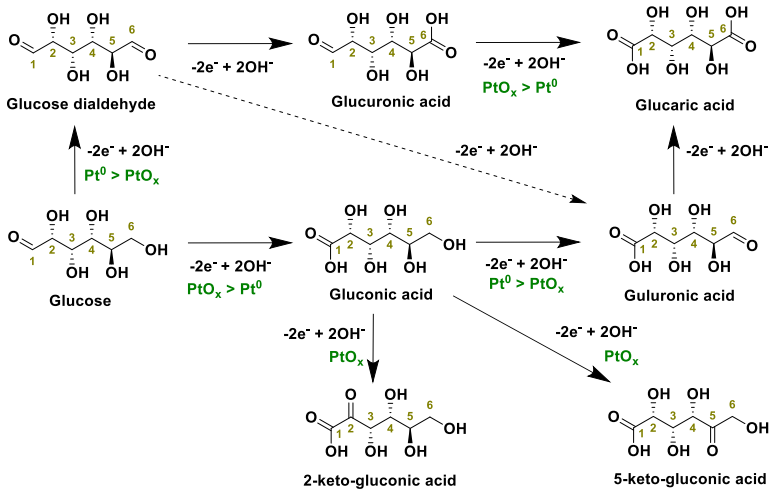
[1] *Biobased Chemistry and Technology, Wageningen University & Research, Wageningen, The Netherlands*
[2] *Catalysis and Surface Chemistry, Leiden University, Leiden, The Natherlands*
harry.bitter@wur.nl

Keywords: Electrocatalytic oxidation, dehydrogenation, glucose, Pt oxidation state, chromatography

Glucose is a highly abundant and sustainable feedstock that can be dehydrogenated and oxidized with Pt electrocatalysts into a large variety of platform and specialty molecules, such as gluconic acid, glucaric acid and 2-keto gluconic acid. The selective production of a single product is one of the key challenges in catalysis and can be improved when the reaction pathway is elucidated.[1] Yet, the glucose oxidation pathway is poorly understood, consequently it remains unclear how the Pt oxidation state affects the electrocatalyst selectivity.

For this study, we 1) combined two analytic methods to quantify all glucose oxidation products, which 2) allowed us to elucidate how the Pt oxidation state affects the dehydrogenation and oxidation of glucose. Glucose (oixdation products) were electrocataytically dehydrogenated/oxidized with a Pt mesh in a divided electrochemical cell at pH = 7 (0.2 M phosphate buffer) at 0.64 V vs. RHE and 1.16 V vs. RHE, corresponfing to metallic platinum (Pt^0) and platinum oxide (PtO_x). The products were quantified by combining high-performance liquid chromatography and high-performance anion exchange chromatography.

Product analysis shows a ~100% carbon balance closure and ~100% faradaic efficiency, indicative that all products were quantified and electrons were retreived. Here we reveal that the glucose oxidation pathway consists of two parallel pathways (Scheme 1). On the one hand, Pt^0 promotes the dehydrogenation of primary alcohol groups, thereby favouring the formation of glucose dialdehyde from glucose and guluronic acid (85%) from gluconic acid. On the other hand, PtO_x promotes the oxidation of aldehyde groups, thereby favouring the formation of gluconic acid (91%) from glucose and glucaric acid (100%) from glucuronic acid. Moreover, PtO_x also promotes the dehydrogenation of the secondary alcohol group of gluconic acid, thereby promoting the formation of 2-keto gluconic acid and 5-keto gluconic acid. These results show that the the Pt oxidation state influences the type of reaction that it catalyzes and thereby be used to steer the reaction pathway for glucose oxidation.



Scheme 1. The electrocatalytic oxidation of glucose at pH = 7 (0.2 M phosphate buffered systems) and the preference of metallic platinum (MPt, E = 0.64 V *vs.* RHE) and platinum oxidation (PtO_x, E = 1.16 V *vs.* RHE).

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Hydrogenation of Biomass-Based Levulinic Acid to γ-Valerolactone Using Supported NiP catalysts

H. Atia[1*], R. Eckelt[1], U. Armbruster[1], S. Wohlrab[1], A. Springer[2], J. Koechermann[3], M. Klemm[3]

[1] *Leibniz Institute for Catalysis, Rostock, Germany*
[2] *Medizinische Biologie und Elektronenmikroskopisches Zentrum Universitätsmedizin, Rostock, Germany*
[3] *Deutsches Biomasseforschungszentrum, Leipzig, Germany*
[*] *udo.armbruster@catalysis.de*

Introduction

The transformation of biomass-based levulinic acid (LA) to γ-valerolactone (GVL) is considered as an attractive biomass conversion route providing GVL as a versatile building block, green solvent, and fuel [1,2]. Finding a cheap and stable catalyst, using water as a solvent, no extra H_2 and reaction temperatures below 200 °C are the main challenges for this reaction. A 2.5%Ru/ZrO_2 catalyst showed a GVL yield of 73% at 150 °C in water (6 h), however, selectivity was too low [3]. On the other hand, 20%Cu/ZrO_2 gave 100% GVL yield at 200 °C within 6 h in a batch reactor in presence of water [3]. In the present work, we tested NiP/SiO_2 in the continous aqueous phase hydrogenation of industrial waste LA in the presence of formic acid (FA) as H-donor.

Experimental/methodology

Home-made NiP/SiO_2 was prepared by reduction of $NiCl_2$ with sodium hypophosphite ($NaPO_2H_2 \cdot xH_2O$) in the presence of colloidal silica. Fresh and spent catalysts were characterized using XRD, ICP, BET SEM and TEM. The reaction was performed in a tube reactor (82 ml) using both model mixtures and an industrial waste stream containing carbohydrates (hydrothermally treated before hydrogenation) in presence of FA. The product was analysed offline with GC and GC/MS, while the gas phase was analysed with online-GC.

Results and discussion

When raising the temperature with a model feed LA/FA = 1:1.2 from 180 to 200 °C, the yield of GVL jumped from 50 to 95% and remained stable for 4 h (WHSV = 6 $g_{feed}/(g_{cat} \cdot h)$). In the further course of the test, the yield slowly decreased to 73% after 72 h on stream (Figure 1a). With the waste mixture (LA/FA = 1:0.4), GVL yield reached 90% at a WHSV = 3 $g_{feed}/(g_{cat} \cdot h)$ and exceeded 50% for more than 20 h (Figure 1b). Deactivation occurred due to structural changes (loss in surface area, Ni leaching) and/or deposition of polymers.

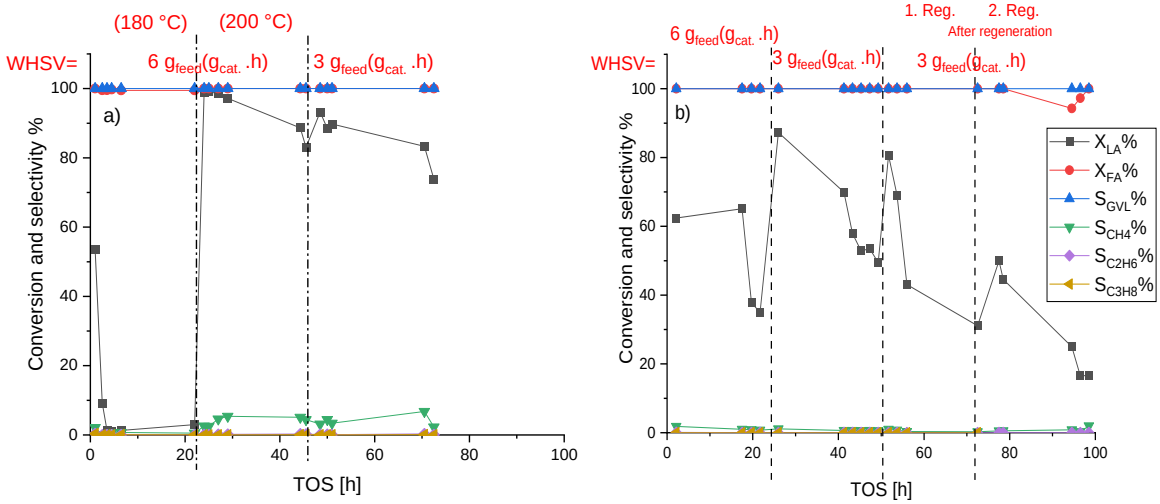

Figure 1: Effect of WHSV on the conversion of LA with 70%NiP/SiO_2 (5 g, 1:2 diluted with quartz) at 200 °C and 30 bar with time on stream using a) model mixture of LA/FA = 1:1.2 and b) waste mixture with LA/FA = 1:0.4.

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Modified SBA-15 materials for the valorization of biomass-derived compounds

J. Aubrecht[1], B. Amin[1], O. Kikhtyanin[2] and D. Kubička[1,2]

[1] University of Chemistry and Technology Prague, Department of Petroleum Technology and Alternative Fuels Technická 5, Prague 6, 166 28, Czech Republic
[2]Technopark Kralupy, Náměstí Georga Karse 7/2, 278 01 Kralupy nad Vltavou, Czech Republic

Key words: SBA-15, modification, synthesis, HMF

Introduction: Ordered mesoporous material SBA-15 (Santa Barbara Amorphous No 15) is an ordered silica having a large surface area reaching up to 1000 $m^2.g^{-1}$. This is due to a channel-type system with a pore diameter of about 5-15 nm. Together with the negligible acid-base character, the large surface area makes SBA-15 a very promising catalytic support. The SBA-15 support can be modified in many different ways, such as by coating the surface with a layer of an oxide having acid-base sites such as TiO_2, ZrO_2 or Al_2O_3. The connection between the high surface area and typical properties of low surface area oxides opens a new chapter of a catalyst support design. Therefore, we investigated the use of SBA-15 as a large surface area template to be coated with different oxides. More importantly, we focused on the formation of an oxide monolayer rather than bulky deposition by standard impregnation.

Methodology: SBA-15 material was synthesized by Zhao procedure (Science 279, 1998). In the synthesis, Pluronic P-123 was used as a structural template and tetraethyl orthosilicate as a source of SiO_2. After that oxides such as TiO_2, ZrO_2 and Al_2O_3 were introduced from organic precursors such as Ti-terc-butoxide, Zr-propoxide or Al-tri-sec-butoxide, respectively, using a different precursor quantity to prepare an oxide monolayer on the SBA-15 surface. After the successful synthesis Ru as the active metal was loaded on these supports. The prepared catalysts were tested in HMF hydrogenation to yield furandiols. All catalysts were characterized using XRF, XRD, TPR, BET, TPD-CO_2 and TPD-pyridine to determine their properties.

Results: The unique set of catalysts was prepared using the oxide-monolayer approach. We proved the successful loading of 10, 30 and 50% of oxides. Despite the high metal oxide loading the material had still a high surface area of over 300 $m^2.g^{-1}$ and accessible pores and channels. The loaded ruthenium made the catalyst active in HMF hydrogenation. We compared all catalysts in terms of activity and compared them with a typical low-surface area SiO_2. The introduction of various oxides changed the acid-base character (probed by TPD techniques) and affected the catalyst selectivity.

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Taking Off with Furfural: Transforming Biomass into Biojet Fuel

R.Baldenhofer [a], J. Lange [a], S.Kersten [a], M.P. Ruiz [a]

[a] *University of Twente, Enschede, Netherlands*

Due to the increasing scarcity and environmental impact of fossil-based fuels, it is becoming very important to search for renewable alternatives. One of the platform chemicals identified to play a key role in the energy transition is furfural.[1] Furfural is an important candidate for the production of jet fuels, among others, and it can be produced from lignocellulosic biomass.[2]

Many different routes for the upgrading of furfural to fuels are known. The most important steps consist of C-C coupling followed by a deep hydrogenation. Different approaches have already been discussed in literature, but most of them lack a cyclic component needed to provide adequate combustion and freeze point properties. A more promising route is to upgrade furfural via the aldol condensation between furfural and cyclopentanone.[3] Using a cyclic component will result in the desired properties which could be used as blend-in fuel.

The challenge of this upgrading route is to obtain cyclopentanone. Besides already existing industrial practices, cyclopentanone can be synthesized from biomass via the reductive rearrangement reaction of furfural, figure 1.[4] Here, furfural is hydrogenated towards furfuryl alcohol, then undergoes an acid catalyzed rearrangement and is subsequently hydrogenated further to form cyclopentanone and cyclopentanol. Understanding and controlling parameters in this reaction could lead to a renewable feedstock for fuels and other applications.

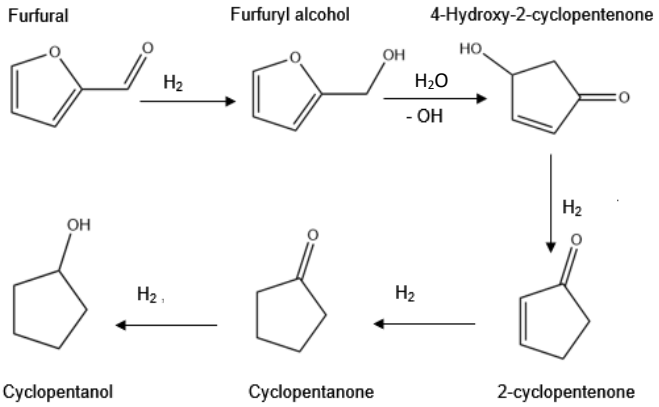

Figure 1: Proposed reaction intermediates for the catalytic reductive rearrangement of furfural to cyclopentanone.

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Catalytic Transfer Hydrogenation of Biomass-based Furfural over Copper Catalyst

Debarun Banerjee[1,2], Aloka Kumar Sahu[1], Jack K. Clegg[2], Sreedevi Upadhyayula[1*]

[1]*Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India*
[2]*The University of Queensland, St. Lucia, QLD 4072, Australia*
[*]*Corresponding Author: sreedevi@chemical.iitd.ac.in*

Keywords: furfural, catalytic transfer hydrogenation, catalyst activation

Introduction. Catalytic transfer hydrogenation of furfural has emerged as one of the most important reactions to yield valuable bio-based chemicals and fuels such as furfuryl alcohol (FAL) and 2-methylfuran (MF) [1]. The conventional catalyst activation process for furfural transfer hydrogenation is limited using extraneous H_2 gas which incurs high infrastructure cost, safety and handling issues [2]. Herein, we report a low-cost and green catalyst activation method which can be highly beneficial for the selective production of MF and FAL from furfural via catalytic transfer hydrogenation with isopropanol as hydrogen donor.

Experimental/methodology. Amorphous silica supported Cu-based catalysts were prepared via the traditional wet impregnation method followed by calcination under static air. The activation of the calcined catalysts was performed under a light source for 2h. In a typical catalytic activity run, the high-pressure batch reactor was filled with a pre-determined quantity of H-donor, furfural, catalyst, and pressurized up to 3MPa with nitrogen after several cycles of purging. Afterward, the reactor was heated to 210°C and kept at that temperature for 4h with continuous stirring. After cooling the reactor, the products were analyzed using nitrogen as carrier gas in a gas chromatograph with capillary column and flame ionized detector.

Results and discussion. The PXRD patterns (Figure-1a) show the prevalence of CuO phases in the calcined catalyst, which underwent reduction to metallic Cu^0 phases during the activation process. The catalytic activity studies (Figure-1b) reveal a steep increase of combined selectivity up to 95% toward FAL and MF by using the activated catalyst compared to the combined selectivity achieved using calcined (21%) and admixed (49%) catalysts. This was due to the formation of Cu^0 sites by activation which promoted hydrogenation and hydrogenolysis of furfural, thereby causing greater selectivity toward FAL and MF. However, the furfural conversion dropped from 75% to 64% while using activated catalyst compared to the admixed catalyst which is attributed to the decrease in synergistic effects of Lewis acidic CuO and metallic Cu^0 sites due to conversion of CuO phases to Cu^0 by activation.

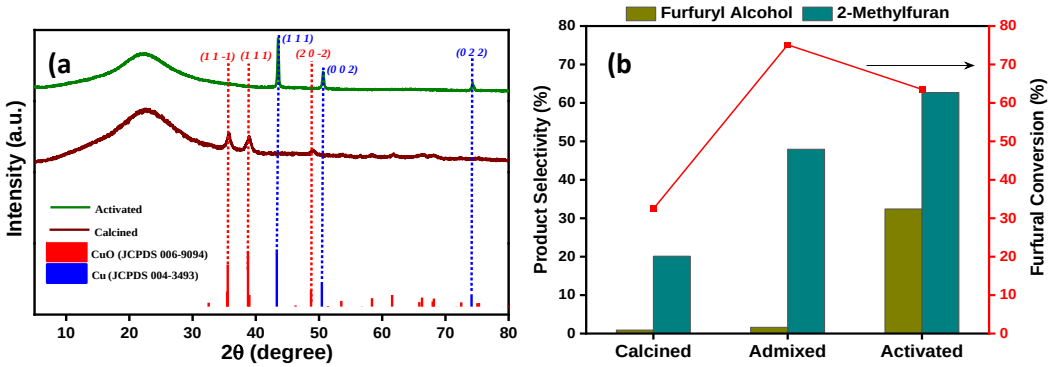

Figure 1. (a) PXRD patterns of the calcined and activated catalysts; (b) Results of catalytic activity studies.

Acknowledgements

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Oxidative Conversion of Lignosulphonates into Vanillin with a Copper–Cobalt Catalyst

S. Bekirovska[1], O. Abdelaziz[1*], C. Hulteberg[1]

[1]*Department of Chemical Engineering, Lund University, SE-221 00 Lund, Sweden*
[*]*omar.abdelaziz@chemeng.lth.se*

Keywords: Catalytic depolymerization, Lignin valorization, Biorefinery, Aromatic chemicals

Introduction.
Lignin, an aromatic polymer constituent of lignocellulosic material, is a vastly underutilized side-stream in the pulp and paper industry as it is commonly incinerated for energy recovery [1,2]. Vanillin is predominantly produced from petroleum-derived guaiacol, as the demand for the chemical exceeds the supply of the vanilla bean [1]. The sustainable production of vanillin and the valorization of lignin could be attained through oxidative lignin depolymerization. This particularly applies to lignosulfonates derived from softwood, where the main product is vanillin since the monomer selectivity is dependent on the botanical origin [3]. The technology dates back to 1937; however, the current process development of oxidative depolymerization is focused on increasing monomer yields and optimizing reaction conditions with, for instance, the addition of catalysts [1,2]. In this work, different metal combinations were tested homogenously using a 50 g/L lignosulfonates solution, which is to be used as a basis for future immobilization.

Experimental/methodology.
A lignosulfonate solution of 20 mL was depolymerized in a 50 mL autoclave at 200 °C and 3 bar O_2 for 10 min (after reaching the operating temperature). The lignin mixture was prepared in a 2 M NaOH aqueous solution with a concentration of 50 g/L. A catalyst loading of 1.4 mmol/g lignin was applied, and eight different homogenous catalyst combinations were tested: Fe-Cu, Fe-Mn, Fe-Co, Cu-Co, Mn-Co, Cu-Mn, Fe-Cu-Mn, and Fe-Cu-Co, with equimolar ratios. A reaction without co-catalyst, i.e. metal catalysts, was also performed and used as the control. A chromatographic system was used for the identification and quantification of the aromatic monomers in the product samples.

Results and discussion.
All the catalyzed reactions resulted in higher yields of total monomers than the control. The highest yields of monomers and vanillin were obtained with the Cu-Co catalyst, having an increased total monomer and vanillin yield of 26% and 24%, respectively, when compared to the control. The immobilized Cu-Co catalyst has been used previously to depolymerize organosolv lignin and has shown considerable breakage of both β-O-4 and carbon–carbon bonds in lignin [5]. To further develop the process into becoming industrially viable, the Cu-Co catalyst needs to be immobilized, and optimization of the operating conditions and catalyst loading needs to be performed. Based on the potentially negative health and environmental effects of both Co and Cu, leaching of the immobilized metals will be a much-studied future topic.

Acknowledgments
This work was supported by the Research Council of Norway through the project L2BA – Lignin to BioAromatics (321427) and the Swedish Foundation for Strategic Environmental Research MISTRA (F2019/1822) within the framework of the research program STEPS – Sustainable Plastics and Transition Pathways at Lund University.

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The Effect of L-Histidine on Enhancement the Fluorescence of Carbon Dots (CD) from *Zingiber Montanum* for Antibacterial and Latent Fingerprint Detection

David Nugroho [1], Suwat Nanan[2], Pooncharat Karittapattawan[3], Saksit Chanthai[2], Rachadaporn Benchawattananon [1,*]

[1]*Department of Integrated Science, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand; davidnugraha95@gmail.com*

[2] Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand.

[3]*Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand.*

**Correspondence: rachadaporn@kku.ac.th (R.B.)*

Keywords: *Zingiber montanum*, Carbon dots, Forensic Science, Antibacterial activity

Introduction : *Zingiber montanum* is a type of natural herbal plant that has high potential medicinal plant as an anticancer, anti-inflammatory, antifungal, antioxidant, anti-allergic and antibacterial, due to the natural ingredients it contains such as Zerembone, Curcumin, etc. Fingerprint is one of the most important types of an evidence in the crime cases because human has different fingerprint mark. Carbon dots (CDs) are a new class of carbon nanomaterials with zero-dimensional carbon based, has the character with sizes below 10 nm and have a three-dimensional structure in the nano regime. The general structure of CDs is sp^3/sp^2, which means CDs can use a fluorescence property that can be applied in various fields such as bioimaging, biosensors, pH sensing, and biomolecule or drug delivery.

Experimental / methodology : Carbon dots (CDs) from *Zingiber Montanum* as a natural source were prepared by hydrotherrmal synthesis methods and applied with starch powder to detect latent fingerprint on non-porous surface materials. In the same way, such nitrogen doped CDs (N-CDs) were also synthesized using one-pot hydrothermal method between *Zingiber montanum* powder and L-histidine. Additionally, the crude extract of *Zingiber Montanum* was used to prepared ZnO photocatalyst as well.

Result and Discussion : Since the N-CDs give rising their fluorescence intensity followed with more brightness under commercial UV lamp compared with bare CDs. The N-CDs were then mixed homogeneously with starch powder and applied on various non-porous material surfaces for latent fingerprint detection, resulted clearer minutiae image compared with black commercial powder under UV lamp. For antibacterial activity, the N-CDs were also applied via agarose disk diffusion assay against various gram-negative and gram-positive bacteria. It was shown that the obtained N-CDs can be high potential use as antibacterial activity as well. In addition, the ZnO photocatalyst preapared from the crude extract of *Zingiber Montanum* was used to degarde the reactive red azo dye. The efficeincy of about 90% was obtained after 90 min of photo irridation.

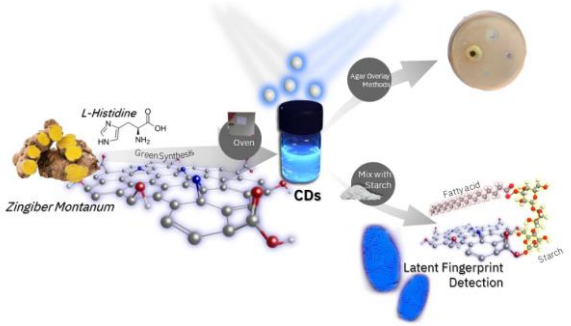

Figure 1. Scheme Synthesis of N-CDS and the application.

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The effect of calcium-based catalysts on deoxygenation of furfural in the production of biomass-derived marine fuels

M. Böhme[1], P.A. Jensen[1], M. Z. Stummann[2], M. Høj[1], A. D. Jensen[1*]

[1]*Technical University of Denmark (DTU),*
Department of Chemical and Biochemical Engineering, Kgs. Lyngby, Denmark
[2]*TOPSOE A/S, Kgs. Lyngby, Denmark*
[*] *aj@kt.dtu.dk*

Keywords: pyrolysis oil upgrading, Hydrodeoxygenation, alternative marine fuels

Introduction. The marine industry contributes a substantial share to the worldwide CO_2 emissions and is expected to grow over the next decades due to an increasing demand for logistics and transportation [1]. Significant reductions in greenhouse gas emissions within this sector along with other hard-to-abate sectors like land and air-based transportation, require innovative and sustainable technologies and fuels in order to meet the necessary targets. Electrification with battery-based technologies faces many challenges for these applications especially regarding the low energy density compared to many liquid fuels [1].

Biomass and plastic waste utilization using catalytic fast pyrolysis to produce oils has experienced increasing interest over the last decades both in fundamental research and industrial application. The crude pyrolysis oil produced typically has a high water and oxygen content leading to a high acidity, low storage stability and low energy density [2]. Removing oxygen-containing groups through catalytic deoxygenation improves the properties and leads to a high value biofuel. It can be mixed with conventional fossil fuels as a drop-in fuel, or it can prospectively replace fossil fuels all together [3].

This contribution focuses on the application of low-cost calcium-based catalysts in the conversion of furfural as a biomass model compound. Different materials including cement raw meal (mixture of $CaCO_3$, SiO_2 and clays), calcined cement raw meal, $CaCO_3$, CaO and $Ca(OH)_2$ were screened as potential catalysts in the catalytic upgrading of pyrolysis oil vapours.

Experimental/methodology. Furfural has been converted with calcium-based catalysts in a mass ratio of 5:1 in a stirred batch reactor at different temperatures from 200 to 300°C in inert atmosphere and at a residence time of 1 h. The liquid product and the spent catalyst were separated, and the oil was analysed using gas chromatography with mass spectroscopy (GC-MS), thermogravimetric analysis (TGA) and elemental analysis.

Results and discussion. $CaCO_3$ and cement raw meal showed little effect on furfural in the whole temperature range, whereas activated basic forms like CaO, $Ca(OH)_2$ and calcined cement raw meal show catalytic activity. Autopolymerisation products of furfural were found at 250°C with increased viscosity and reduced oxygen content. At 300°C, using CaO and $Ca(OH)_2$ total conversion towards gas and char under strong temperature and pressure increase took place. This shows the high activity of calcium-based materials as low-cost catalysts in deoxygenation of biomass-derived compounds, whilst further research on the application of these catalysts in pyrolysis oil upgrading is ongoing.

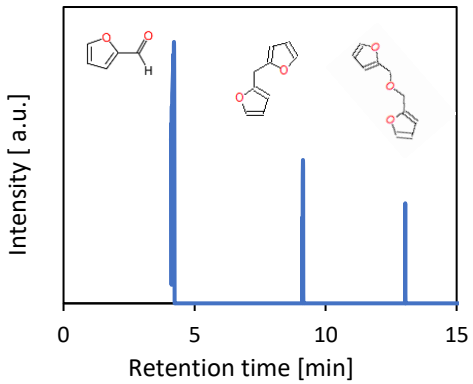

Figure 1: Gas-chromatograph mass-spectrometer analysis of the liquid phase of converting furfural with calcined cement raw meal at 250 °C.

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Pyrolysis and hydrotreatment of Kraft Lignin: Cu-based catalyst for pyrolytic oil hydrodeoxygenation

M. Borella[1,2], M.A. Palazzolo[2], H.H. van de Bovenkamp[2], P.J. Deuss[2] , A.A. Casazza[1], G. Garbarino[1*], G. Busca[1]

[1] *Department of Civil, Chemical, and Environmental Engineering, University of Genoa, Genova, Italy.*
[2] *Department of Chemical Engineering, ENTEG, University of Groningen, 9747 AG Groningen, The Netherlands*
[*] *Corresponding Author:Gabriella.Garbarino@unige.it*

Keywords: Lignin, Pyrolysis, Oil upgrade, Catalytic Hydrotreatment

Introduction.

Kraft lignin is one of the most produced lignin available on the market, and it is produced as a side-product of the paper industry[1], [2]. Moreover, Kraft lignin presents a relevant amount of S whose content represents an obstacle to its valorization. Pyrolysis of lignin is one of the most powerful methods used for its depolymerization, aimed at the production of aromatics[3]. The oil produced from pyrolysis is rich in phenol-like compounds, but further upgrading is needed to make the pyrolysis oil (Pyoil) suitable for future applications[4], [5]. In this project, a first step of pyrolysis has been conducted, and after the characterization of the oil, Cu/TiO_2 catalysts have been used to address the production of phenolic-like monomers[6].

Experimental/methodology.

The pyrolysis setup consisted of a steel reactor where 30g of lignin have been loaded and heated up to 550°C for 20 minutes. Vapors produced during the process have been cooled down in three different steps in series with water, ice, and liquid nitrogen, respectively. Part of the sulfur presents in the raw biomass still remained in the oil in the form of disulfides and thiophenes. For this reason, a catalytic test has been performed on a model compound, 4-methyl-guaiacol, adding thiophene as an external sulfur source in order to see the influence of sulfur on the activity of the catalyst. Cu/TiO_2-P25 catalytic activity in the presence of different amounts (wt.%) of sulfur has been studied. The catalyst Cu/TiO_2-P25 (0.100 g) and SiC support (0.200 g) were loaded into the reactor and reduced *in situ* at 360°C at 6 bar of H_2 pressure for 2 hours. The tests have been performed using a down-flow reactor for a Time of Stream (TOS) of 4h in the same conditions. Hydrodeoxygenation (HDO) tests have been conducted at 300-350°C, and 100 bar of H_2 pressure using the Pyoil as reagent in presence of 0.5g of Cu/TiO_2.

Results and discussion.

The yield of pyrolysis oil obtained is around 30 wt.%, the char around 35 % as well as non-condensable gas calculated by difference. GC-MS analysis showed a wide range of alkyl-phenol compounds, where 4-methyl guaiacol was one of the most abundant ones. These results have been confirmed from ^{13}C NMR, while Gel Permeation Chromatography showed good depolymerization of the raw biomass and good data reproducibility. Cu/TiO_2-P25 was active for the demethoxylation of 4-methyl guaiacol with either 0.1 wt.% and 1 wt.% sulfur. The reaction products mainly consist of methyl, dimethyl, trimethyl, and tetramethyl phenols. An increase in the amount of sulfur slightly affects the conversion. HDO tests of the Pyoil showed a decrease in the content of methoxy phenols of 10%, , and an increase of alkylated (methyl, dimethyl and trimethyl) phenols from 1.2 to 6.5%. Dealkylation does not occur during HDO and phenols lacking alkyl substituents are unreactive.

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Development of Ni-Mo catalysts supported on silica for the transformation of residual fatty raw materials into green diesel

J. Zafeiropoulos[1], G. Petropoulos[1], E. Kordouli[1,2], C. Kordulis[1,2], A. Lycourghiotis[1,2], K. Bourikas[1,*]
[1]*School of Science and Technology, Hellenic Open University, Patras, Greece.*
[2]*Department of Chemistry, University of Patras, Patras, Greece.*
[*]*bourikas@eap.gr*

Keywords: Selective Deoxygenation, Green diesel, Ni-Mo Catalysts, Silica, Residual fatty raw materials

Introduction

A great source of renewable energy is biomass comprised from natural triglycerides, which contain smaller amounts of oxygens compared to other kinds of biomass. The selective deoxygenation (SDO) is an attractive upgrading process for this kind of biomass [1,2]. It is realized by hydrotreatment through decarboxylation ($deCO_2$), decarbonylation (deCO) and hydrodeoxygenation (HDO). In this context, two types of catalysts are proved to be very effective: supported noble metals and conventional sulphided NiMo, CoMo and NiW supported catalysts. However, both kinds of catalysts present several weaknesses. The noble metals have high cost and limited availability. On the other hand, the conventional sulphided NiMo, CoMo and NiW catalysts need to be maintained in the sulphided form by introducing sulphur compound in the feed, which presumably results to S-contaminated end products. The aforementioned weakness motivated, in the last years, intensive research on the less expensive transition metal catalysts in their metallic, phosphide, and carbide forms [2]. In this context, we developed Ni-Mo catalysts supported on silica with different atomic ratios of Ni/(Ni+Mo), in order to find the optimum ratio for the best peroformance of the catalysts in the the catalytic deoxygenation of sunflower oil towards green diesel. In the next step, we evaluated the best catalyst in the transformation of residual fatty raw materials (RFRMs) such as Waste Cooking Oil (WCO), Free Acid Distillates (FAD), Chicken Oil (CHO) and Spent Coffee Ground Oil (SCGO), into green diesel.

Experimental/methodology

A series of 4 catalysts ($NiMo/SiO_2$) was prepared using the wet impregnation technique, with various atomic ratios of Ni/(Ni+Mo) (0.84, 0.91, 0.95, 0.98). For comparison, the corresponding monometallic catalysts were also prepared. All catalysts had total metal loading equal to 50 wt %, since this has been found the optimum one in Ni/SiO_2 catalysts concerning SDO [3]. $[Ni(en)_3]^{2+}$ was used as the precursor Ni complex (where en stands for ethylenediamine) and ammonium heptamolybdate was used as the Mo precursor. In all cases, the deposition of the active phases was followed by drying, calcination and reduction. The physicochemical characteristics of the catalysts were studied using various techniques, such as N_2 adsorption-desorption, XRD, TPR, NH_3-TPD and TGA. The evaluation of the catalysts was performed in a semi-batch reactor at the following conditions: ratio of feed to catalyst mass 100 ml / 1 g, pressure 40 bar, H_2 flow rate 100 ml / min, speed of stirring 2000 rpm, temperature 310°C. A liquid sample was withdrawn from the reactor every hour and analyzed on a GC-MS system. The reaction was monitored for a period of 9h.

Results and discussion

All catalysts proved very active and selective in the SDO of sunflower oil to green diesel. The optimum ratio of Ni/(Ni+Mo) was found equal to 0.95. The promoting effect of Mo is due to its interaction with Ni, which significantly improves its dispersion, to the increase of the moderately acidic sites of the catalyst and to the creation of oxygen vacancies that appear in the molybdenum oxide and accelerate the SDO mechanism. The best catalyst, with the optimum Ni/(Ni+Mo) ratio, proved very effective also in the SDO of the residual fatty raw materials. The end products were mainly normal alkanes in the diesel range (n-C15, n-C16, n-C17, n-C18). The composition of the reaction liquid mixture in total green diesel follows the order: 92% (CHO), 90% (WCO), 68% (FAD) and 16% (SCGO). The comparison made between fresh and used NiMo catalyst showed that the coke deposit on the surface of the latter is significantly smaller compared to that of the Ni catalyst and the reduction in its active surface was relatively small. The above indicate that this catalyst maintains its physicochemical characteristics to a satisfactory degree and is quite stable even after a long time of reaction.

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Influence of natural mordenite activation mode on its efficiency as support of nickel catalysts for biodiesel upgrading to renewable diesel

K. Fani[1], S. Lycourghiotis[1], K. Bourikas[1], E. Kordouli[1,2*]

[1]*School of Science and Technology, Hellenic Open University, Patras, Greece*
[2]*Department of Chemistry, University of Patras, GR26504, Patras, Greece*
[*]*ekordouli@upatras.gr*

Keywords: biodiesel upgrading, green diesel, biofuels, Ni catalysts, natural mordenite treatment

Introduction.

In nowadays there is a rapid increase in the energy requirements of modern societies due to the growing population as well as the modern way of life. On the contrary, we are ever closer to the exhaustion of fossil fuels, the use of which is inextricably linked to climate change phenomena. This has alarmed the global scientific community, which is in constant search for renewable fuels. Biodiesel is such a fuel existing already in the market. The production of biodiesel via transesterification in microalgae and subsequent extraction appears to be a promising process in the future for biodiesel production. However, the biodiesel produced cannot be used as a direct substitute for conventional diesel and it needs to be upgraded. The development of cheap catalysts for this process is a key research task [1]. The present work focuses on the nickel catalysts development exploiting a Greek natural zeolite, mordenite, as a catalytic support. Two activation modes (acid and acid/alkali treatment) were tested for improvement of supporting properties of natural mordenite. The Ni catalysts prepared were evaluated for biodiesel transformation to green diesel at various reaction temperatures.

Experimental/methodology.

Natural mordenite from a Greek island [2] was treated with HCl aqueous solution (2M, 70 °C, 4h, mass / volume: 1/20) and then the solid was dried (110 °C overnight) and calcined (500 °C, 2 h), MO_A. An aliquot of MO_A sample was treated with NaOH aqueous solution (2M, 65 °C, mass / volume: 1/15) and then exchanged with NH_4NO_3 aqueous solution (1M, 80 °C, 24h). Finally, it was dried and calcined as mentioned before, MO_{AB}. Two Ni catalysts (30 wt % Ni) were prepared using the activated supports by deposition-precipitation method ($NiMO_A$, $NiMO_{AB}$). XRF, N_2-physisorption, XRD, TEM, SEM, H_2-TPR, NH_3-TPD were used for catalysts characterization. A semi-batch high pressure (4MPa) reactor was used for catalysts evaluation.

Results and discussion.

Figure 1 shows that $NiMO_{AB}$ catalyst proved the most efficient one resulting in 94 % hydrocarbons (green diesel) yield after 9 h at 350 °C. Its high efficiency is attributed to the higher surface area, higher Ni^0 surface, moderate acidity related with lower coke formation, and its resistance to thermal sintering in comparison with the $NiMO_A$ catalyst. The hydrocarbons produced had one carbon atom less than the corresponding fatty acids being in biodiesel feed. Free fatty acids (Acids in Fig. 1) and high molecular weight esters (Esters in Fig. 1) are intermediate products upon biodiesel hydrotreatment.

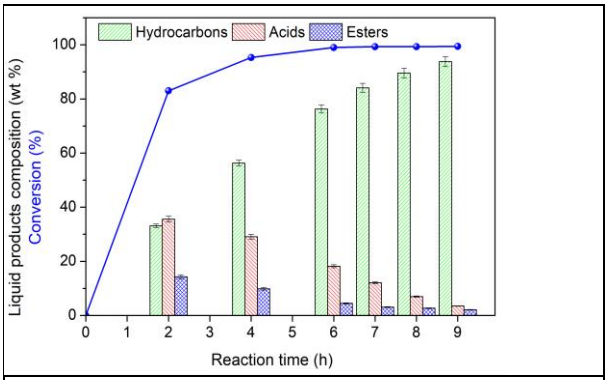

Figure 1. Catalytic performance of $NiMO_{AB}$ catalyst

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Promoted nickel catalysts supported on palygorskite for green diesel production

Fani K.[1], Lycourghiotis S.[1], Kordouli E.[1,2], Kordulis C.[1,2], Bourikas K[1,*].
[1]*School of Science and Technology, Hellenic Open University, Patras, Greece*
[2]*Department of Chemistry, University of Patras, Patras, Greece*
[*]*bourikas@eap.gr*

Keywords: Palygorskite, Promoted nickel catalysts, Green diesel, Waste cooking oil, Selective deoxygenation.

Introduction.

Beyond doubt our society is dealing with the depletion of fossil fuels in which there is a worldwide dependence as a main energy source. It is clear that a very promising approach is the use of biofuels. Green diesel can become a great potential to be a sustainable replacement for fossil fuel through selective deoxygenation of waste cooking oils (WCO) [1]. Additionally large amounts of catalysts will be essential in order to enhance the production of biofuels. Efforts of using cheap and abundant minerals as carriers for heterogenous catalysts have aggregated the interest of scientists [2]. In this work, nickel catalysts, promoted by different metals (Mo, W) supported on the natural cheap mineral palygorskite, were evaluated for green diesel production.

Experimental/methodology.

The raw material palygorskite was cleaned by a clay fraction method in order to be discharched of contaminants. Three nickel catalysts were synthesized via deposition-precipitation method with urea as precipitation agent: one monometallic catalyst with 30 wt. % nickel loading (30NiPal), a molybdenum promoted catalyst with Ni/(Ni+Mo)=0.95 (30NiMoPal) and a tungsten promoted catalyst with composition similar to the aforementioned one (30NiWPal). Both promoted catalysts had also30 wt. % total active phases loading. The final catalysts were obtained by reduction of the catalysts precursors with H_2 stream (30 mL/min) at 500°C for 2.5 hours. The reduced catalysts were characterized using nitrogen adsorption-desorption isotherms, XRD and NH_3-TPD. Precursor samples (before reduction) were characterized by H_2-TPR. 30NiPal and 30NiMoPal were evaluated in the SDO of WCO at 310 ^{o}C, hydrogen pressure 40 bar and reactant volume to catalyst mass equal to 100 mL / 1 g. Then, 30NiMoPal was evaluated to four different temperatures 330, 350, 370 and 390 ^{o}C. At optimal temperature, 370 ^{o}C, the amount of catalyst was duplicated in order to maximize green diesel production. Likewise at aforementioned conditions (T=370°C, reactant volume to catalyst mass 100 mL/2g), the 30NiWPal catalyst was evaluated for comparison reasons.

Results and discussion.

Comparing monometallic Ni catalyst with the Mo-promoted Ni one, we found that the addition of molybdenum as a promoter enhanced significantly the production of hydrocarbons in the range of diesel (C_{15}-C_{18}) in the liquid product (from 23 to 45 wt %). This is attributed to the well known promoted action of Mo [3] as well as to the increase of the active surface of Ni in the promoted catalyst. Concerning the ideal temperature of the SDO reaction with the 30NiMoPal catalyst, it proved to be 370 ^{o}C, where a value of 80% in hydrocarbons in the liquid product was achieved. In the same temperature, double mass of catalyst was examinated and green diesel in the liquid product reached 90%. Concerning the W-promoted Ni catalyst, at the same conditions, the evaluated 30NiWPal catalyst produced the same amount of hydrocarbons as the 30NiWPal catalyst. These results demonstrate similar promoting action of tungsten with molybdenum, which has been also observed in other catalytic systems [4]. Taking into account these results, Mo(W)-promoted nickel catalysts supported on palygorskite could be successfully used as low cost and very efficient natural catalysts for green diesel production from waste cooking oils.

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Synthesis of ion-exchange-resins-based bifunctional catalysts for MIBK one-pot production

E. Canadell, J.H. Badia, R. Soto, R. Bringué, E. Ramírez, J. Tejero

Chemical Engineering and Analytical Chemistry Department, Universitat de Barcelona, Barcelona, Spain

Introduction. Due to environmental concerns, the research for renewable alternatives to petrol-based derivatives has increased significantly. Among many potential candidates, methyl isobutyl ketone (MIBK) has drawn certain attention since it is a value-added chemical that can be obtained from acetone through a three-step catalytic pathway, including aldol condensation, dehydration and hydrogenation reactions [1,2]. Bifunctional acidic ion exchange resins, such as Amberlyst^{TM}CH28 (ACH28), have exhibited promising results, in terms of yield and selectivity, allowing to carry out the MIBK synthesis under mild conditions throughout a one-pot synthesis approach [1,3]. To enhance our knowledge on such synthesis, in the present work, the commercial ion exchange resins (Amberlyst^{TM}15 and Dowex 50Wx2), have been doped by wet impregnation with noble (Pd and Ru) and non-noble (Cu) metals and are tested in the MIBK reaction.

Experimental/methodology. The bifunctional catalysts were prepared by simple wet impregnation. In a typical experiment, 40.0 g of acetone and 2.0 g of the dried bifunctional catalyst, in the unreduced form, were loaded to a 100 mL stainless-steel batch reactor (316 SS Autoclave Engineers, Inc). Then, the air was removed with three N_2 flushing cycles. Afterwards, the N_2 was replaced with H_2. Temperature was set at 120 °C and stirring speed at 300 rpm. The reactor pressure was kept constant at 30 bar with H_2. The reaction mixture was analyzed by gas chromatography, after the reaction time.

Results and discussion. Pd-doped catalysts were the most active ones. Among them, Dow2-1%Pd showed the highest yield (36.8 %) to MIBK, a similar value as the obtained with the commercial ACH28 (see Table 1).

Table 1. Experimental results (120 °C, 20 bar, 300 rpm, 5 wt.% catalyst loading, 4 h).

Catalyst	$X_{acetone}$ [%]	S_{MIBK} [%]	Y_{MIBK} [%]	ICP-MS [M wt.%]	TON [mol acetone converted/ mol M]
ACH28 (Pd)	35.2	100	35.2	0.70	1839
A15-1%Pd	30.9	100	30.9	0.95	1190
A15-1%Ru	15.1	39.2	5.9	1	527
A15-1%Cu	10.3	9.8	1.00	0.91	244
Dow2-1%Pd	36.8	100.0	36.8	0.89	1500
Dow2-1%Ru	16.4	27.2	4.46	1	571
Dow2-1%Cu	16.1	5.329	0.861	0.92	385

By comparison of the prepared catalysts, it can be observed that gel-type (i.e, Dow2), achieved higher acetone conversion at the expense of lower selectivity, than for macroporous resins (i.e, A15). Comparing the different metals, the noble doped catalysts resulted in a better performance than the non-noble metal doped ones. Pd-doped ion exchange resins performed better than those doped with Ru because Pd can hydrogenate C=C groups while Ru is mainly used for hydrogenating CO groups. Furthermore, the palladium leaching hardly took place during the reaction while the copper content decreased significantly (above 80%), indicating that leaching was at play. Additionally, the acid capacity of the resins did not change, indicating that no loss of acidic sites took place during the reaction.

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Hydrogenation of 4-(2-furyl)-3-buten-2-one to jet-fuel precursors using hydrotalcites

Claudio C. Díaz[1*], Ana B. Dongil[2], Néstor Escalona[1]

[1]*Pontificia Universidad Católica de Chile, Santiago, Chile*

[2]*Instituto de Catálisis y Petroleoquímica, Madrid, España*

* *cicontreras6@uc.cl*

Keywords: Hydrogenation, hydrotalcites, ceria, zirconia, Jet-Fuel

Introduction. The use of lignocellulosic waste, such as forest residues and sawdust, is especially attractive as a sustainable and economically resource. Hemicellullose is one of the major components of non-edible biomass which can be transformed into C_5-C_6 sugars, and further used to produce several chemical reagents [1]. Furfural, which is obtained by dehydration of glucose, is widely used as platform molecule and one application is the aldol condensation with ketones to grow carbon chains and produce jet fuel or value-added products[2]. Hydrotalcites (HTC) are lamellar materials of general formula $Mg_6Al_2CO_3(OH)_{16}$, known as aldol condensation and hydrogenation catalysts. In this work we aim at studying the effect of Ce and Zr as modifiers, in the hydrogenation of 4-(2-furyl)-3-buten-2-one using isopropanol as green solvent.

Experimental/methodology. Modified hydrotalcites were prepared by co-precipitacion method using nitrates of $Cu_{1.5}$:$Mg_{1.5}$:Al_{1-x}:M_x (M = Zr or Ce, X=0.1 or 1). Samples were then calcined in air at 500 °C for 2 h, and reduced at 500 °C under H_2. Catalytic experiments were conducted in a batch Parr reactor. Catalysts have been characterized by XRD, SEM, H_2-TPR, N_2-adsorption.

Results and discussion. The XRD of reduced hydrotalcites (Fig.1) show the characteristic HTC spinel peaks at 2θ = 43° and 63° which are sharper for CuMgZr and CuMgAlZr, this suggesting that these samples hold a more homogeneous structure. All the samples displayed the diffraction due to Cu(0) except CuMgAlCe. Interestingly, for this latter sample the incorporation of Ce leads to CeO_2, while this is not observed in CuMgCe. The initial rate (Fig.2) was estimated at 20% conversion and followed the trend: CuMgCe >CuMgZr>> CuMgAlZr ~CuMgA>CuMgAlCe. For all the catalysts, the C=C bond hydrogenation is the preferred path, while hydrogenation of C=O increases slightly with Ce. Selectivity towards D and D_2 (OH cyclation of D and hydrogenation of the ring) increases as Al in HTC is replaced by Ce or Zr. Overall, activity significantly improves by the incorporation of Ce or Zr into the HTC. Despite the selectivity differences are modest, they suggest that Ce favors the hydrogenation of the C=O bond. Nevertheless, the effect of the solvent seems to be critical in the reaction, and further investigations are being performed.

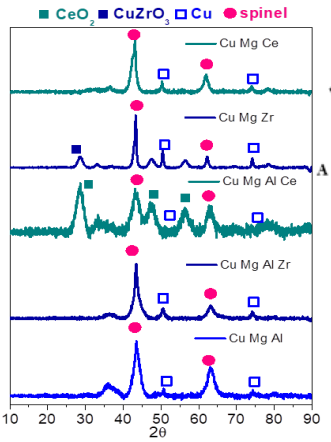
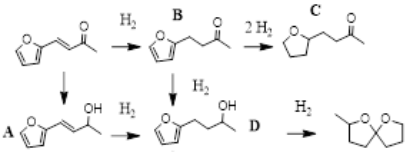


Figure 1. XRD of modified



Scheme 1: Proposed reaction pathway

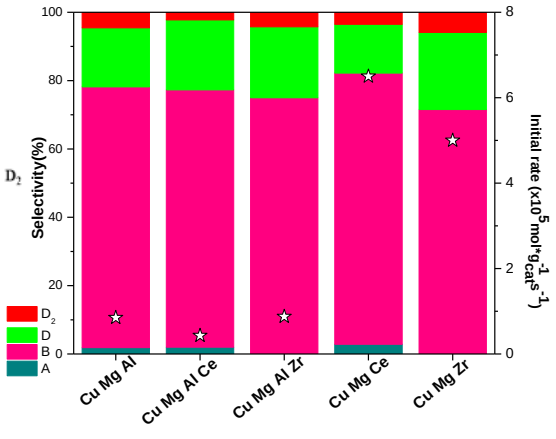


Figure 2: Selectivity and Initial rate at 20% conversion, 30 MPa H_2 at 150°C

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Selective H_2 production from formic acid decomposition over Re and Mo supported catalysts

Claudio C. Díaz[1], N.Escalona[1], I. Rodríguez-Ramos[2], A. B. Dongil[2*]

[1]*Pontificia Universidad Católica de Chile, Santiago, Chile*

[2]*Instituto de Catálisis y Petroleoquímica, Madrid, España*

**a.dongil@csic.es*

Keywords: H_2 production, Formic acid decomposition, Rhenium Oxide

Introduction. Hydrogen is an energy vector and a main reagent to synthesize high value-added compounds. However, 96% of H_2 worldwide is obtained from non-renewable resources. In this context, biomass-derived compounds like HCOOH (FA) are interesting as a renewable source since it is easier to manipulate, transport and store than H_2 [1]. Recently, molybdenum carbide supported on carbon materials, has been evaluated as catalyst for FA decomposition with high selectivity to CO_2 at low temperatures [2]. So far, Re has been used successfully in several hydrodeoxygenation reactions, but no studies have been done in formic acid decomposition. In this work, we have evaluated the effect of the support morphology, i.e. Graphite (G) vs carbon nanotube (CNT), and synthetic atmosphere on the obtained metal phase. The catalysts were tested on the decomposition of formic acid.

Experimental/methodology. Catalysts were prepared by impregnation with 10% wt. metal over commercial carbon supports (CNT O^+ and HSAG 400 (G)), and treated under 3 different atmospheres: C_2H_4/H_2 (25/75), H_2 and N_2 at 650°C, 650°C and 350°C, respectively. Experiments were performed in a fixed-bed reactor using FA (3.25% vol.) diluted in He with a WHSV of 10.8 mL FA $g_{cat}^{-1}min^{-1}$ at different temperatures.

Results and discussion.

In situ XRD of Re/G-H_2 displayed characteristics peaks of Re(0) at 2θ=36°, 40° and 42° while Re/G-N_2 presented peaks at 37°, 54° and a broad hump at 43° due to ReOx. Mo/G-H_2 showed diffractions at 2θ = 37° and 53° which could be assigned to MoO_xC_y and MoO_2 phases. From these results, it seems that Mo is carburized by gasification of the support while Re is carburized just under C_2H_4/H_2. Regarding reaction results, Re is the most active and most selective to CO_2 reaching ~94-98% selectivity while Mo-based catalysts reached 86-89%. Both Re/G-H_2 and Re/G-N_2 yielded similar results despite the different phase obtained. The support with better conversion was the graphite. In summary, unlike Mo, Re oxide which is synthetized at low temperature under inert gas can decompose FA at low temperatures. This is relevant to further use the obtained H_2 for hydrodeoxygenation reactions, for which ReOx has proved to be very active.

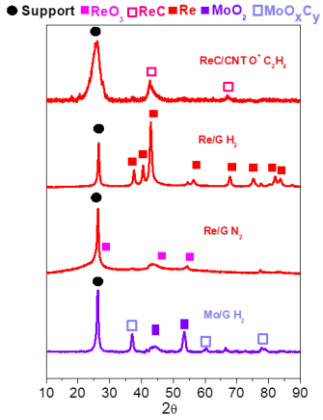

Fig.1: In situ XRD under H_2 or N_2

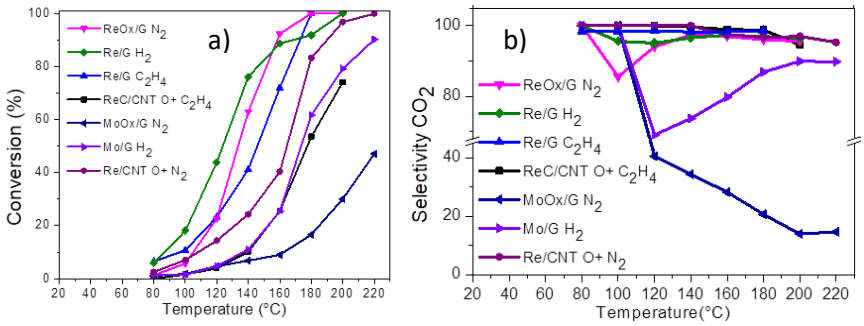

Fig. 2: a) Conversion of HCOOH; b) Selectivity to CO_2

Acknowledgements

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Epoxidation of tall oil in presence of heterogeneous catalysts

T. Cogliano[1,2*], A. Desgouliere[1,3], W. Y. Perez-Sena[1], K. Eränen[1], V. Russo[1,2], L. Pirault-Roy[3], T. Salmi[1]

[1]*Åbo Akademi, Åbo-Turku, Finland*
[2] *Università Degli Studi di Napoli "Federico II", Naples, Italy*
[3]*Université de Poitiers, Poitiers, France*
[*]*tommaso.cogliano@abo.fi* – *tommaso.cogliano@unina.it*

Keywords: Tall oil Epoxidation, Heterogeneous Catalysis, Catalytic Screening

Introduction. Epoxidized Vegetable Oils (EVOs), thanks to the highly reactive epoxy group are excellent molecular platforms. EVOs have already been used to obtain polyols, carbonates and plasticizers [1]. Industrially, epoxidation of vegetable oil is carried out in semi-continuous mode via the Prilezhaev process where a percarboxylic acid acts as the oxidant agent by shuttling an oxygen atom from the polar aqueous media to the organic apolar one [2]. Despite its wide application, the process suffers from several drawbacks due to the use of homogeneous mineral acids to catalyze the formation of the percarboxylic acid, sas well as low selectivity toward the target product, demanding separation steps and corrosion of the reaction and separation equipment. To overcome this problem, different heterogeneous catalysts have been tested in both the epoxidation via the Prilezhaev process and the presence of hydrogen peroxide, looking for a catalyst with activities and selectivity at least comparable to the homogeneous ones [3]. In the present project, we have focused our attention on the epoxidation of tall oil, a Scandinavian raw material originating from Kraft pulping process, in the presence of heterogenous catalysts and hydrogen peroxide as the oxidizing agent. The main aim is to find the best catalyst in terms of activity and selectivity as well as to work in presence of a bio-based, non-toxic solvent which can improve or at least replicate the performance of the selected catalyst replacing the environmentally unfriendly ones.

Experimental/methodology. The adopted strategy is at first select and synthesize several promising heterogenous catalysts after which all of them are tested in the epoxidation process with a fatty acid model compound looking for the most promising one. Finally, the selected catalysts are studied in the epoxidation of tall oil by changing several experimental parameters, i.e. temperature, double bond-to-H_2O_2 molar ratio and solvent, as well as the amount of catalyst and amount of specific active phase on it. The goal is to achieve good performances in terms of activity, selectivity and reusability of the selected catalyst by studying in depth the relationship between the physicochemical properties of it and the obtained performances in the reaction system.

Results and discussion. The present project aim to study a new promising catalyst for the epoxidation of vegetable oil (tall oil) in the presence of hydrogen peroxide as oxidizing agent and bio-based solvent. The final aim is to shift to a renewable reaction system where all the reaction elements, namely reactants, solvent and catalyst, are either by-products from other reaction system or are renewable, non-toxic and environmentally friendly compounds following the idea of green chemistry and circulary economy.

Acknowledgments
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One-pot method of production carboxylic acids from hemicellulose-derived mixture of sugars over Na-BEA zeolite.

N.Sobuś[1], I.Czekaj[1*]

[1] *Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Krakow, POLAND*
**izabela.czekaj@pk.edu.pl*

Keywords: Na-BEA zeolite; Catalysis; Biomass; carboxylic acids; Oxalic acid; Lactic acid; Levulinic acid

Introduction

The purpose of the process is to develop a method for obtaining C1–C5 carboxylic acids (levulinic acid, oxalic acid, lactic acid, and formic acid) from a mixture of C6 and C5 carbohydrates derived from waste lignocellulosic biomass – hemicellulosic fraction using the one-pot method. We present the conditions for the conversion of hemicellulose with different contents of C6 and C5 carbohydrates and uronic acids based on the OrganoCat process [3].

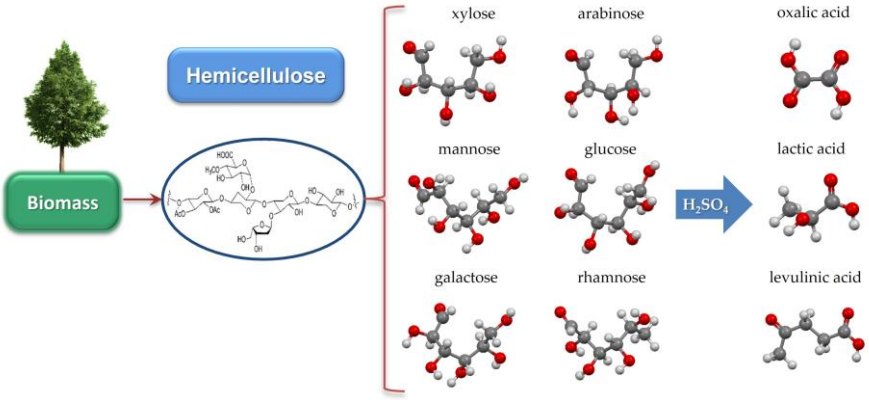

Fig. 1. Valorization of hemicellulose-derived mixture of sugars to carboxylic acids.

Experimental/methodology.

Three hemicellulose sugar mixtures were investigated, with different ratios of xylose, mannose, galactose, glucose, rhamnose, galacturonic acid and glucuronic acid (Figure 1). Three heterogeneous catalysts were used: Na-BEA zeolite and two ion exchange resins (AMBERLYST 15(H), DOWEX DRG8(H)). The one-pot catalytic conversion of fructose was performed in temperature ranges 100-250 °C for 1-5 h. Identification of products formed in the post-reaction mixture were identified with the participation of HPLC-RID.

Results and discussion.

Lactic acid (LAC) was obtained with the maximal yield of 86,4% (5 h, 250°C, DOWEXDR8X(H)) and levulinic acid (LA) with the yield of 44.1% 5 h, 250°C, DOWEXDR8X(H)) with the participation of DOWEXDR8X(H) as catalyst.

Acknowledgments

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One pot glycerol valorization of glycerol into acrylic acid: a catalytic and spectroscopic study

A. De Arriba[1], D. Delgado[1], P. Concepción[1], J. M. López Nieto[1,*]

[1]*Instituto de Tecnología Química, UPV-CSIC, 46022 Valencia, Spain*
[*]*jmlopez@itq.upv.es*

Introduction.
Multifunctional materials based on Nb/V-doped hexagonal tungsten bronzes (HTB) have demonstrated to be outstanding catalysts in the glycerol dehydration to acrolein [1]. Additionally, molybdenum based mixed oxides presenting the so-called M1 phase showed interesting properties in the partial oxidation of propane [2] and acrolein [3] to acrylic acid. Therefore, the aim of this work is to study the effect of using a single or double bed configuration by combining these two families of catalyts in order to optimize the selectivity to acrylic acid in a one pot aerobic transformation directly from glycerol.

Experimental/methodology.
Nb/V-doped HTB (*h*-$W_{0.71}Nb_{0.29}O_3$ and *h*-$W_{0.8}V_{0.2}O_3$) and M1 (MoVO, MoVTeO and MoVTeNbO) catalysts have been prepared hydrotermally at 175°C/72h and finally heat-treated afterwards at 550 (tungsten bronces), 400 (MoVO) or 600°C (MoVTeNbO) for 2h under N_2 stream. The physicochemical characterization of these oxides includes: XRD, NH_3-TPD, N_2-adsorption, Raman and XPS spectroscopies. *In situ* IR studies of adsorbed intermediates have been also carried out over selected catalysts. In addition, the catalytic tests were carried out in a fixed-bed reactor (alterning one or two subsequent catalytic beds) at 320°C and ambient pressure, with products being analyzed by both liquid and gas cromatography [3].

Results and discussion.
Characterization results indicate that both Nb^{5+} and V^{5+}/V^{4+} enter the HTB structure through isomorphic substitution of the Me^{n+} cations for lattice W^{5+} (**Fig. 1A**), while M1 oxides displayed differences in the XRD peaks, related to dissimilar shape of the crystals (**Fig. 1A**). However, regarding the catalytic results, for a single bed configuration, modified hexagonal tungsten bronces showed a selectivity to acrolein (*h*-$W_{0.71}Nb_{0.29}O_3$) and acrylic acid (*h*-$W_{0.8}V_{0.2}O_3$) notoriously higher than M1 catalysts (**Fig. 1B**). Nevertheless, by using a double bed configuration consisting of a first acidic bed (*h*-$W_{0.71}Nb_{0.29}O_3$) followed by an oxidizing bed (M1-phase catalysts), excellent catalytic performance can be achieved by modulating the second bed (**Fig. 1C**), with tetrametallic M1-MoVTeNb oxide presenting the best results (yield to acrylic acid up to 65%). The nature of active sites is also discussed by considering the *in situ* IR studies of adsorbed acrolein.

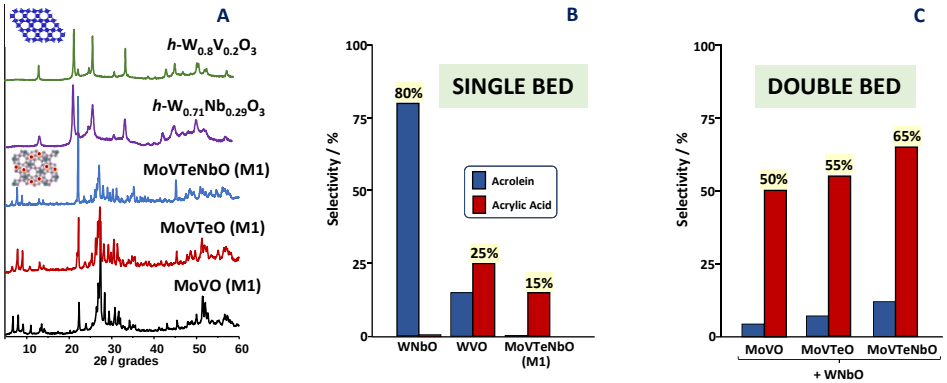

Figure 1. XRD patterns (**A**) of both Nb/V doped-Hexagonal Tungsten Bronze and M1-MoV(Te,Nb)O catalysts, and selectivity to acrolein/acrylic acid at 100% glycerol conversion of selected W- and Mo-based bronze catalysts in single (**B**) and combined bed (**C**) configurations.

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Efficient two-step production of biobased plasticizers: Dehydration-hydrogenation of citric acid followed by Fischer esterification

Anthony De Bruyne[1], Wouter Stuyck[1], Willem Deleu[2], Jarne Leinders[1], Carlos Marquez[1], Kwinten Janssens[1], Dimitrios Sakellariou[1], Ruben Ghillebert[2] and Dirk E. De Vos*

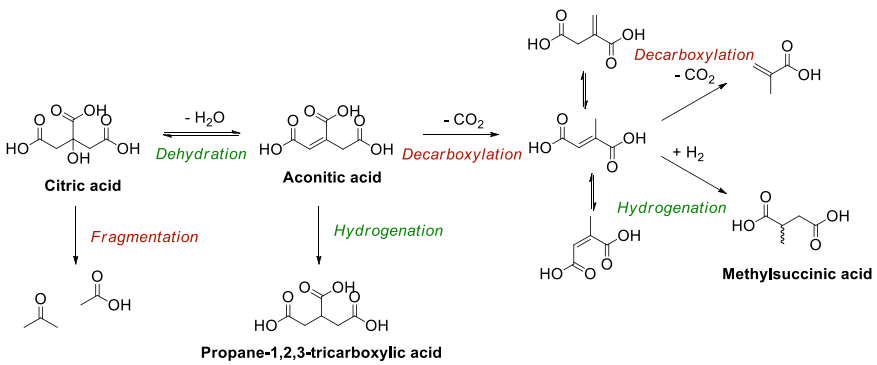
[1] *KU Leuven, Leuven, Belgium,* [2] *Citribel, Tienen, Belgium ,** *dirk.devos@kuleuven.be*

Keywords: Catalysis, Biomass to chemicals

Introduction. The increase in the global plastic consumption is accompanied by a growing concern about the safety of these plastics and their additives. For example, ortho-phthalates, which were the traditional plasticizers of polyvinyl chloride (PVC) plastics, are suspected to be bio-accumulating and endocrine disrupting.[1] A promising, safe and green alternative are derivatives of the renewable citric acid. Here, we focus on the production of propane-1,2,3-tricarballylate plasticizers, which possess excellent plasticizing properties.[2,3]

Experimental/methodology. In a first step, dehydration-hydrogenation reactions of a large amount of CA (20 mmol) were performed at relatively mild reaction conditions (150°C and 20 bar H_2) using $Al_2(SO_4)_3$ (homogenous) combined with Pd^0/C (heterogenous) as a catalytic system and water as a green solvent. In a second step, the reaction mixture was transferred to a Dean-Stark setup in order to perform a Fischer esterification with n-butanol, during which the previously used $Al_2(SO_4)_3$ could be recuperated. Reaction mixtures were anlysed *via* ^{1}H-NMR.

Results and discussion. In this work, $Al_2(SO_4)_3$ in combination with Pd^0/C was found to be a cheap, stable and well-performing alternative to catalyze the dehydration-hydrogenation of citric acid. Citric acid and Al^{3+} ions are known to strongly interact resulting in aluminum citrate (Al-citrate) complexes.[4] Both citric acid conversion and PTA yield were maximized at a pH value of 1.1 - 1.3. Through investigation by ^{27}Al NMR and ^{1}H-NMR, it was observed that under the applied conditions Al-citrate complexes are mainly present as $[Al\text{-}Hcit]^+$ and $[Al\text{-}cit]^0$. This may suggest that these species are the most active for the dehydration of citric acid. A maximum PTA yield (93%) was achieved for a reaction of 1 M citric acid (in 20 mL water), 1.25 mmol $Al_2(SO_4)_3$ and 0.5 mol% Pd^0 (Pd^0/C) with 20 bar H_2 at 150 °C for 20 hours (initial pH of 1.16). Only small amounts of methyl succinic acid (see Figure) were detected as side product. The stability of the $Al_2(SO_4)_3$ and Pd^0/C catalyst was confirmed by a fed-batch experiment and by CO chemisorption. Additionally, the catalytic system was proven to be robust, since the PTA yield remained largely unaffected when an industrial post-fermentation process stream (containing multiple organics and inorganics) of citric acid was used as substrate for the process.



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An innovative catalytic pathway for the synthesis of acyl furanics: the cross-ketonization of methyl 2-furoate with carboxylic acids

Jacopo De Maron[1,2], Davide Cesari[1],Tommaso Tabanelli[1,2], Andrea Fasolini[1,2], Francesco Basile[1,2], Fabrizio Cavani[1,2].

[1] *Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Bologna, Italy*
[2]*Center for Chemical Catalysis-C3, Università di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy*
[*]*jacopo.demaron2@unibo.it*

Keywords: 2-acetyl furan, methyl 2-furoate, cross-ketonization, continuous-flow, gas-phase.

Introduction. In recent years, the ketonization of carboxylic acids has emerged as a main way to valorize multiple biomass-derived products. For instance, the coupling of light acids has been extensively investigated for the H_2-free deoxygenation of the bio-oils from fast-pyrolysis of lignocellulose [1], while the ketonization of fatty carboxylic acids (vegetable oils or waste fat) produces bio-based lubrificants and/or waxes [2]. However, the full potential of this reaction has yet to be suitably developed, in particular aimed to the alternative production of valuable asymmetric ketones.

In this work, the cross-ketonization between methyl 2-furoate (MF) and acetic acid (AA) was investigated with the aim of selectively synthesizing 2-acetyl furan (AF), a well-known flavour/fragrance and pharamaceutical intermediate [3]. This approach towards AF (depicted in figure 1), in respect to the traditional Friedel-Crafts acylations with homogeneous Lewis acid catalysts, would benefit from continous operation, a much easier work-up, and the use of bio-based feedstocks (e.g. AA and furfural-derived MF).

Experimental/methodology. All catalytic tests were carried out in the gas-phase using a continous-flow fixed-bed reactor. Unreacted reactants and products were quantified by means of GC-TCD (online) and GC-FID (offline). Unknown products were identified by means of GC-MS. Monoclinic ZrO_2 was prepared adapting a precipitation technique from the literature [4].

Results and discussion. The synthesis of AF was preliminarly carried out over ZrO_2 by feeding an AA/MF/N_2 = 1/1/98 mixture at 350 °C, contact time = 1 second. In these conditions MF conversion was ≈ 70 % and AF yield was ≈ 43 %; at the same time, AA conversion was complete, meaning that the homo-ketonization of AA towards acetone competed with the desired reaction, subtracting AA and limiting the achievable yield of AF. Therefore, the excess of AA in respect to MF was increased by increasing the molar fraction of AA in the feed up to 4 %: in these optimized conditions the conversion of MF was complete and a 70 % yield of AF in respect to MF was achieved. The versatility of this synthetic route towards acylfurans was further investigated by carrying out the cross-ketonization between MF and carboxyilic acid with different chain-lenghts (i.e. propionic and butyric acid), thus extending the substrate scope of the method to the propionyl- and butyryl-derivatives of furan, which were obtained with 70 and 80 % yield respectively.

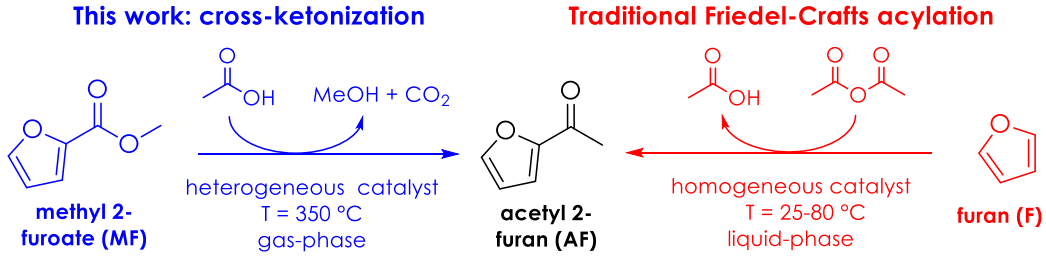

Figure 1: AC synthesis by means of cross-ketonization between MF and AA compared to the traditional synthesis by means of Friedel-Crafts acylation of furan with acetic anhydride.

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Catalytic Valorisation of Furans to Aromatics over Modified Zeolites

G.J.L. de Reijer[1*], A. Schaefer[1], A. Hellman[1], P.A. Carlsson[1]
[1]*Chalmers University of Technology, Gothenburg, (Sweden)*
**guidod@chalmers.se*

Keywords: Biomass conversion, 2,5-dimethylfuran, Gallium, Ga-silicate, ZSM-5, BEA

Introduction

The growing demand for a sustainable chemical industry can be satisfied by utilizing renewable carbon sources like lignocellulosic biomass. One interesting model reaction is the conversion of biomass-derived furans into valuable aromatic building blocks such as benzene, toluene, and xylenes (BTX). Microporous solid acid catalysts, such as zeolites and zeotypes, are employed for their readily tuneable acidity and porosity, for example through incorporation of heteroatoms.

Experimental/methodology

For the conversion of 2,5-dimethylfuran (2,5-dmf) into BTX, a continuous fixed-bed powder reactor is used in which the effluent gases are analysed using using an online mass spectrometer (MS) as well as an online Fourier Transform Infrared (FTIR) spectrometer. Advantages of using this continuous reactor and on-line analysis is the high sampling frequency of at least 4 min^{-1}, as well as the ability to co-feed addends like ethene and propene in a stepwise manner. Zeolitic and zeotypic catalysts are prepared through a broad variety of synthesis methods. Structural analyses of fresh and spent catalysts and their acid sites include XRD, XRF, N_2/Ar-physisorption, SEM, TEM, EDX, TGA/DSC, NH_3-TPD, DRIFTS, and ^{29}Si-, ^{27}Al-, ^{71}Ga-MAS NMR.

Results and discussion

To examine the effect of incorporating heteroatoms into the catalyst and its ability to convert furans into aromatics, aluminium and gallium have been isomorphously substituted into MFI framework silicalite-1, resulting in ZSM-5 and Ga-silicate, respectively [1]. These heteroatoms proved crucial for creating active sites and Ga-silicate demonstrated a superior BTX selectivity and catalyst lifetime, compared to ZSM-5 catalysts with both an equal or higher acid site density. The catalysts of relative low acid site densities remained active for isomerisation reactions even after 10 hours of 2,5-dmf conversion at 500 °C, whereas conversion to BTX was below 5% after 2 hours on stream. Acid site analysis before and after the reaction revealed deactivation of strong, extra-framework acid sites, associated with the cracking, decarbonylation and dehydration of the reactant 2,5-dmf which provided an unsaturated olefinic hydrocarbon pool (fig. 1). Co-feeding of ethene did not influence the BTX formation, suggesting the absence of a Diels-Alder Cycloaddition-Dehydration mechanism.

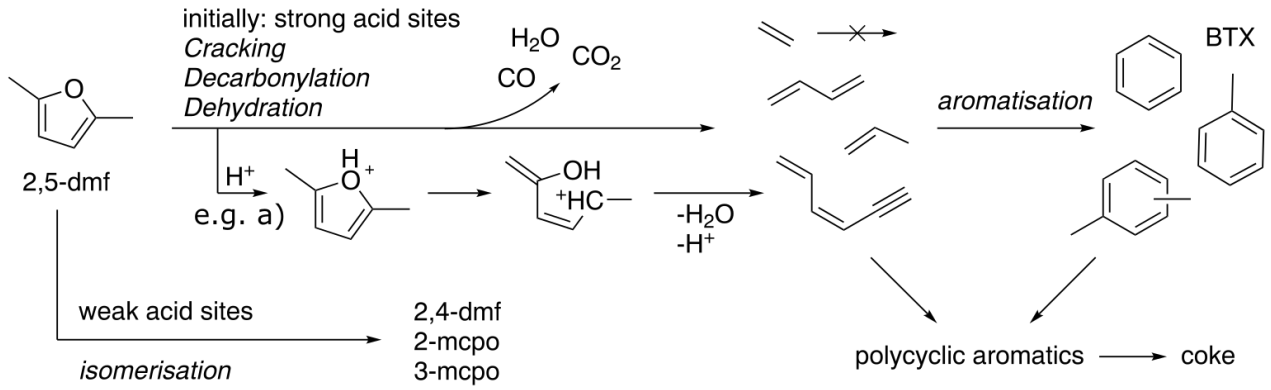

Fig. 1: Reaction scheme for the conversion of 2,5-dmf [1]. Possible pathway a) was suggested by Uslamin et al [2].

Acknowledgments

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Promotion Effect of $KHCO_3$ on Palladium Hydride Catalyzed Decarboxylation of Aryl-aliphatic Acid

Fuli Deng[1], Ruixue Zhao[1], Andreas Jentys[1], Yue Liu[1,*], Johannes A. Lercher[1,3*]

[1] *TUM School of Natural Sciences, Technische Universität München, Garching, Germany.*

[2] *Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, Washington, United States*

[*] *johannes.lercher@ch.tum.de*

Keywords: Decarboxylation, Pd catalysts, Promotion effect, Alkali-metal compounds.

Introduction. Direct converting carboxylic acids into high-valued alkanes by hydrodeoxygenation is an effective way to achieve the upgrading of biomass-derived chemicals to high-value fuels. Developing efficient methodologies for conversion of carboxylic acids into alkanes under relatively mild conditions is essential for carboxylic acids utilization[1]. Alkali metals were found to be effective modifiers for the catalysts in various reactions by adjusting the surface acid-base property, increasing dispersion and stability of host metals (such as Pt, Pd, Cu, Co, etc.,), and participating in reaction[2,3] . Therefore, in this work, we report an efficient decarboxylation of carboxylic acids by modifying PdHx/C[4] catalyst with $KHCO_3$, which can greatly enhance the decarboxylation activity and is applicable to various carboxylic acids and the promotion mechanism is also investigated.

Experimental/methodology. Pd/C and alkali-metal compounds modified Pd/C catalysts were synthesized by the incipient wetness impregnation method. Catalytic decarboxylation reactions were performed in a high-pressure stainless-steel autoclave (300 mL) with a mechanical stirrer and a heating jacket. In situ sampling was carried out during the reaction by taking 1 mL of reaction liquid through a sampling tube with a filter. GC-MS analyzed the products. Reaction mechanism The physical and chemical properties of the catalyst were characterized by N_2 adsorption, H_2-Chemisorption, CO/CO_2-TPD, XRD and XANES.

Results and discussion. Decarboxylation of hydrocinnamic acid on PdH_x/C exhibited poor activity with a TOF of 5 h^{-1}. When introducing a small amount of alkali metal compounds to the Pd/C surface, the decarboxylation performance of PdH_x/C undergoes obvious changes (**Fig. 1**). By screening different potassium compounds including KOH, K_2CO_3, $KHCO_3$ and KCl, 1wt. % $KHCO_3$ modified PdH_x/C exhibits the highest decarboxylation activity (TOF of 96 h^{-1}) which is almost 20 times higher than the unmodified PdH_x/C catalyst. CO_2-TPD reveals that the introduction of $KHCO_3$ enhances the surface basicity. RCOO-K species was identified from XRD profile of used catalyst, deuterium labeling results indicate COOH group of the reactant is preferably adsorbed and dissociated on the $KHCO_3$–modified catalytic surface. Therefore, the promotion effect of $KHCO_3$ on the PdH_x/C catalyst could be ascribed to that $KHCO_3$ activates the COOH group by reversibly reacting with the proton in COO-H and forming hydrocinnamate anion intermediate (COO*). This dissociatively adsorbed hydrocinnamate anion is reported to be more preferable for the C-C bond cleavage than the molecularly adsorbed carboxylic acid, thus contributing to a higher decarboxylation activity on $KHCO_3$-modified PdH_x/C catalyst.

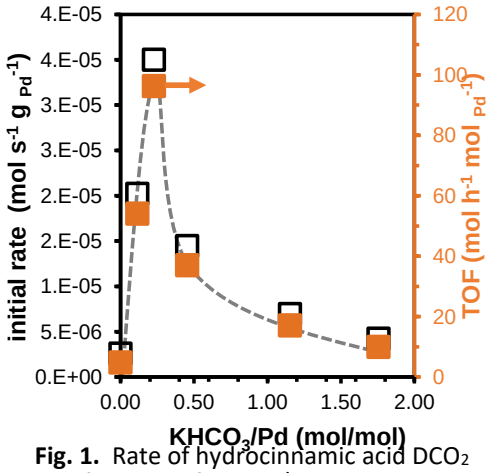

Fig. 1. Rate of hydrocinnamic acid DCO_2 as a function of $KHCO_3$/Pd molar ratio.

Acknowledgments

The authors would also like to thank Lehrstuhl für Technische Chemie II technicians for their help in catalyst characterization. And also thank Juanjuan Huang from the Munich Compact Light Source (MuCLS) of Technical University of Munich for the related XAS measurement. F.D. would like to thank the Chinese Scholarship Council for its financial support.

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Lignocellulose to ethylene glycol: catalyst poisoning

T.D.J. te Molder,[1] S.R.A. Kersten,[1] J.-P. Lange,[1,2] M.P. Ruiz[1]
[1]*Sustainable Process Technology, University of Twente, Enschede, The Netherlands*
[2]*Shell Global Solutions International B.V., Amsterdam, The Netherlands*
e-mail: jean-paul.lange@shell.com

Introduction.
To mitigate climate change and decrease society's reliance on fossil resources, the industry must develop new processes to produce fuels and chemicals from renewable carbon resources. One of them is the hydrogenolysis of carbohydrates to ethylene glycol (EG). This reaction exploits a tandem catalyst system based on homogeneous WO_x and heterogeneous Raney-Ni; the former cleaves the sugar to glycol aldehyde and the latter hydrogenates the glycol aldehyde to EG. This reaction proceeds with good selectivity with clean glucose and cellulose, but with lower yields with lignocellulose. We will discuss here this challenge and assign it to complex catalyst deactivation by feedstock contaminants, i.e., partly by lignin and more critically by ash and S/N. Catalyst deactivation is indeed a critical, though often neglected challenge in biorefining [1].

Results.
The yield loss observed with real lignocellulosic feedstock has been assigned to catalyst poisoning because it is avoided by using excessive amounts of WO_x and Ni catalysts in batch operation.
The first suspected poison is lignin that accounts for ~25 wt.% of lignocellulose. Experiments with delignified feedstock and physical mixtures of cellulose/lignin confirmed some poisoning of the raney-Ni catalyst by lignin [2]. However, they could not assign the yield loss to lignin: some lignin-rich feed reached high EG yields while some lignin-lean ones did not.
We then turned to the ash that can account for <10 wt.% of lignocellulose. We removed part of the ash by various wash treatments and added some to clean cellulose [3]. Divalent cations, particularly Ca^{2+}, appeared to consume WO_x by converting it to inactive $CaWO_4$ precipitate (fig. 1, left).
But the Ca content still failed to explain the very low EG yield measured with some grasses in the presence of excess WO_x. Beyond being rich in Ca (~0.1 wt.%), grasses can also contain ~1 wt.% of N and ~0.1 wt.% of S, e.g., bound in proteins. Deep removal of N and S by water/acid wash indeed allowed hay to deliver EG yields that are comparable to that of clean cellulose (fig. 1, right) [4].

This study allowed us to define quality criteria for hydrogenolysis feed. It also allowed us to propose a pretreatment scheme to help bringing real lignocellulosic feedstock up to specification [5].

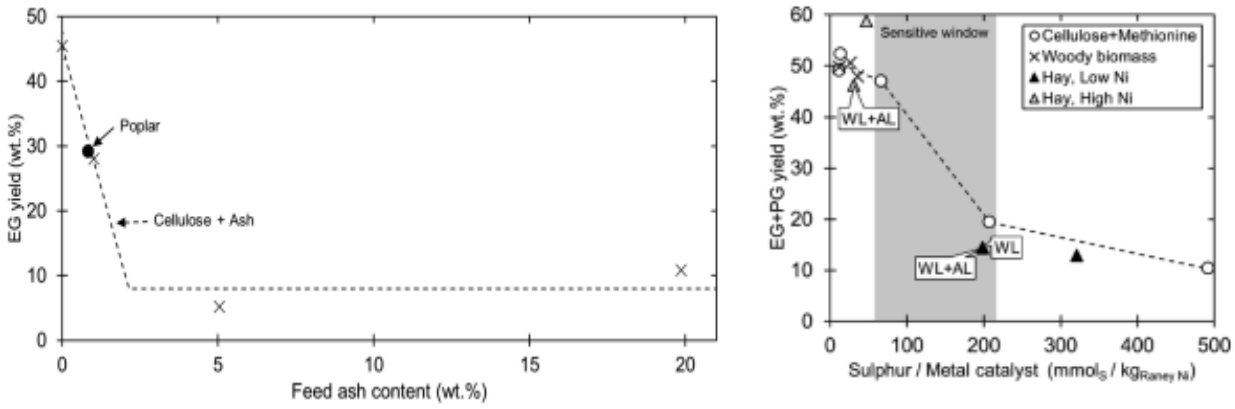

Figure 1 – Ash and S poisoning of cellulose hydrogenolysis to ethylene glycol (EG)

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Triacylglycerides to marine and jet biofuel via hydrotreating

A. Dimitriadis[1*], V. Vasdekis[1], C. Kekes[1], S. Bezergianni[1]

[1]*Centre for Research & Technology Hellas (CERTH),*
Chemical Process and Energy Resources Institute (CPERI) Thessaloniki, 57001, Greece
[*]*adimitr@certh.gr*

Keywords: Biofuels, hydrotreatment, marine biofuel, Jet biofuel, Triacylglycerides

Introduction.
The global aviation industry seems to be a constantly and rapidly expanding sector in recent years. The International Air Transport Association (IATA) claims that the request for air connectivity will continue to grow. In addition in April 2018, IMO's Marine Environment Protection Committee (MEPC) adopted an initial strategy on the reduction of greenhouse gas emissions from ships.The major challenge for thermochemical pathways is to develop conversion technologies with reduced energy consumption. In this direction, it is critical the incorporation of alternate approaches aiming to supply the demanding energy requirements of gasification process, syngas production, purification, hydrocracking etc. [1]. The BioSFerA concept aims to develop a combined thermochemical - biochemical pathway that minimizes the shortcomings of the existing technologies and takes advantage of their strong aspects in order to produce elevated yields of the desired fuels with limited energy consumption[2].

Experimental/methodology.
The overall process, combining thermochemical, biological and thermocatalytic parts is based on the gasification of biomass and other biogenic waste in a Dual Fluidized Bed gasifier and the 2-stage fermentation of the produced syngas. Through this process the syngas is converted to acetate (1st stage) and then the acetate is converted to TAGs (2nd stage). The produced TAGs contained medium and long fatty acids were hydrotreated and isomerized after the necessary separation and purification and the end-products are jet- and bunker-like biofuels, respectively. The current manuscript, will present the step of TAGs upgrading via hydroprocessing targeting jet- and bunker-like biofuels.

Results and discussion.
The results have shown that the most influential parameter during hydrotreatment, is the reaction temperature that strongly affects the mass recovery curve of the product. In general, higher reaction temperatures favour hydrocracking reactions leading to lighter hydrocarbons in jet fuel range. On the other hand, lower hydrotreating temperature leads to heavier hydrocarbons in bunker fuel range. Thus, the choice of reaction temperature is very important as it affects the final distillation range and thus the bunker fuel and jet fuel yields of the product. Pressure is also influencing the hydrotreating reactions and more specifically, the higher the pressure the lighter the product is. However, the effect of pressure is not as strong as that of temperature. Furthermore, as higher pressures and temperatures favour hydrocracking reactions, this result in higher hydrogen consumption. The hydrogen consumption increased as the heavier hydrocarbons are cracking to lighter ones. Thus, the choice of the optimum operating parameters is very important and depends first of all from the targeted products (bunker or jet range biofuels) and also from the optimum hydrogen consumption.

Acknowledgments
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Copper-cobalt ferrites supported on carbon-containing porous matrices as catalysts for syngas production from methanol

M. Dimitrov[1*], G. Issa[1], S.P. Marinov[1], N. Velinov[2], B. Tsyntsarski[1], D. Kovacheva[3], J. Tolasz[4], J. Henych[4]

[1]*Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*
[2]*Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria*
[3]*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*
[4]*Institute of Inorganic Chemistry of the Czech Academy of Sciences, Řež, Czech Republic*
[*]*Momtchil.Dimitrov@orgchm.bas.bg*

Keywords: copper-cobalt ferrites; methanol decomposition, activated carbon, ceria-carbon hybrids

Introduction.

Nowadays, methanol is considered as an important hydrogen precursor and carrier as hydrogen can be easy and safely released from it at relatively low temperatures by simple catalytic process of metanol decomposition. This reaction gives as products a gaseous mixture that can contain H_2 , CO, CO_2 and CH_4. In order to lead the reaction selectively to syngas production a very important role plays the used catalyst. Bulk transition metal containing ferrites show high ability to decompose methanol predominantly to syngas [1,2]. However, if we use a high surface area support, we could improve activity, selectivity and stability of the active phase using just a small amount of it. Carbon-based supports have many advantages, such as high surface area, well-developed porous structure and tunable surface chemistry, stability at high temperatures in inert or reduction atmosphere. Additional improvement of both textural and chemical functionality could bring the combination of nanostructured ceria with carbon materials (nanodiamond or graphene oxide). The aim of the present study is to show the advantages of using $Cu_{0.5}Co_{0.5}Fe_2O_4$ supported on various carbon-containing supports as catalysts for syngas prtoduction from methanol.

Experimental/methodology.

For the preparation of the catalysts were used as supports three activated carbon materials synthesized from various mixtures based on spent motor oil and sawdust, coal and fly ash, respectively, as well as ceria-carbon hybrids (ceria-graphene oxide and ceria-nanodiamond). The copper-cobalt ferrites ($Cu_{0.5}Co_{0.5}Fe_2O_4$, total metal content of 8 wt %) modifications were prepared by incipient wetness impregnation from the corresponding metal nitrate precursors. The obtained final catalysts were characterized by a complex of characterization techniques (X-ray diffraction, nitrogen physisorption, Moessbauer spectroscopy, and temperature-programmed reduction with hydrogen) and their ability to decompose methanol was studied as well.

Results and discussion.

The obtained results show a fine dispersion of the supported active phase in all studied samples, and it represents a complex mixture of species in different oxidation state. The active phase udergoes changes during the reaction due to the reductive influence of the reaction medium that reflects in both activity and selectivity of the catalysts. At low conversion temperatures (500-600 K) the selectivity to syngas production reaches above 90 % and gradually decreases to about 70 % with further temperature increase up to 750 K. At the same time the activity varies among the studied materials and seems to be significantly influenced by the support textural and functional characteristics.

Acknowledgments

This project has received funding from Bulgarian National Science Fund, project КП-06-Н27/9, and the European Regional Development Fund within the Operational Programme Science and Education for Smart Growth 2014–2020 under the Project Center of Excellence: National center of mechatronics and clean technologies- BG05M2OP001-1.001-0008. The bilateral project IC-CZ/04/2020-2022 between BAS and Czech Academy of Sciences for scientific support is also acknowledged.

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Selective Dehydration of Xylose catalyzed by Metallic Mixed Oxides

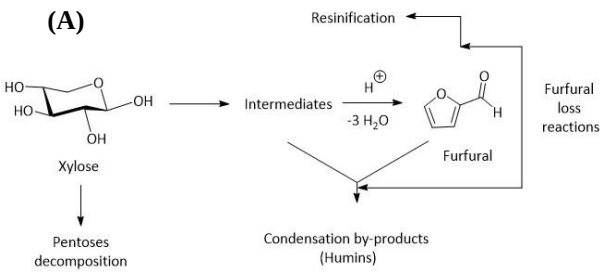
Francisco Cernicharo-Toledo[1], Agustín De Arribas[1], José M. López-Nieto[1], Marcelo E. Domine[1*]
[1]*Instituto de Tecnología Química, Universitat Politècnica de València, Consejo Superior de Investigaciones Científicas, Avda. Los Naranjos S/N, 46022, Valencia, Spain*
[*]*mdomine@itq.upv.es*

Keywords: C5 sugars, xylose dehydration, furfural, acid catalyst, metal mixed oxide.

Introduction. Nowadays, the depletion of petroleum resources combined with the increasing demand for fuels and energy from emerging economies, and political and environmental concerns about fossil fuels, makes imperative to develop economical and energy efficient processes for the sustainable production of fuels and chemicals. Thus, plant biomass is the only renewable source of carbon and Hydrogen for biofuels and biochemicals production.[1] Furfural is a biomass-derived chemical considered as a platform chemical for fine chemicals industry, as well as useful for many other applications, such as extractant in the refining of lubricating oils, fungicide precursor, nematocide, adhesive, etc.[2] Furfural is produced from agricultural/waste raw materials rich in hemicellulose (pentosan polymers) by depolymerisation of pentosan to pentoses (mainly xylose) at high temperatures (150-250 ºC) in the presence of acid catalysts (i.e. sulfuric acid). Nevertheless, industrial processes suffer from serious drawbacks (i.e. corrosive and toxic catalysts or humins deposits), and technological improvements are needed to increase the possibilities of furan-based chemical industry. In this work, different metallic mixed oxides with controlled acid and textural properties are used as catalysts for selective dehydration of xylose to furfural, and their catalytic activity compared to homogeneous (i.e. H_2SO_4) and heterogeneous (i.e. zeolites) reference catalysts.

Experimental/methodology. Metal oxides and mixed oxides were prepared by co-precipitation or by hydrothermal synthesis from the corresponding metal precursors, characterized by ICP, XRD, N_2 adsorption isotherms, SEM and TEM, NH_3-TPD), and calcined in air at 450-550 ºC prior to their use as catalysts. Catalytic tests were performed in a 12 mL teflon-lined autoclave reactor equipped with a magnetic stirrer, temperature and pressure controllers and a valve for liquid/gaseous sample extraction. Typically, 10wt% xylose in water or H_2O/alcohol mixture and the solid catalyst were poured into the reactor. The reactor was closed and the xylose dehydration was performed at 160 ºC during 3 h under continuous strirring. After cooling to room temperature, the reaction mixture was filtered and liquids analysed by HPLC (Agilent 1200 with RI detector and a Bio-Rad Aminex HPX-87H column, with 5 mM H_2SO_4 as mobile phase at 60 ºC).

Results and discussion. Different solid acid materials based on transition metal oxides and mixed oxides were synthesized and essayed in the xylose dehydration to furfural, and their catalytic activity was compared to the both homogeneous (H_2SO_4) and heterogeneous (zeolites, commercial oxides) reference catalysts (Fig. 1B). The xylose dehydration goes through intermediates formation giving furfural as main product if the catalyst offer the adequate acidity, but intermediates rapidly undergo non-desired reactions (condensation, resinification) if active sites have lower or higher acidity than required (Fig. 1A). Among the different metallic oxides tested, Nb-based mixed oxides with adequate combination of Brönsted and Lewis acid sites give results (in terms of conversion and selectivity) similar to H-USY zeolite, higher than other single metal oxides, and close to those achieved with sulfuric acid industrial catalyst.



(B)

Results at 80-100% of conversion

Entry	Catalyst	Xylose Conversion (%)	Selectivity to Furfural (%)
1	H_2SO_4	85.4	44.8
2	H-USY	99.8	34.0
3	WO_3	89.9	26.2
4	Nb_2O_5	80.8	14.5
5	WZr-O	85.0	23.6
6	WV-O	90.4	23.7
7	WNb-O	95.1	36.7

Humins as main sub-products, acetic acid, formic acid and formaldehyde in minor amounts.

Figure 1. A) Reaction network for furfural synthesis via hydrolysis/dehydration of xylose; B) Catalytic results at 80-100% conversion.

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Hydrogen production through aqueous phase reforming of ethanol using molybdenum carbide catalysts supported on zirconium

C. Pavesi[1,2*], E. Blanco[1,2], C. Pazo[1,2], A.B. Dongil[3], N. Escalona[1,2]

[1]*Pontificia Universidad Católica de Chile, Santiago, Chile*
[2]*Millenium Nuclei of Catalytic Processes towards Sustainable Chemistry, Santiago, Chile*
[3]*Instituto de Catálisis y Petroleoquímica CSIC, Cantoblanco, Spain*
[*]*capavesi@uc.cl*

Keywords: molybdenum carbide, aqueous phase reforming, hydrogen production

Introduction. Recently, there has been a growing interest in revaluing residues generated by biorefineries in order to reduce their environmental footprint. Hydrogen production using biomass derivatives has been studied through vapor phase reforming or supercritical water reactions [1]. Ethanol is an atractive precursor and transition metal carbides, such as molybdenum, have catalytic potential to replace noble metals both in vapor and water phases [2]. In this work, aqueous phase reforming (APR) was studied to value ethanol in hydrogen, using molybdenum carbides in two cristaline phases (α y β) supported on zirconium. Carburization temperature (650-700°C), metal content (5-10-15% Mo) and reaction temperature (225-250-275°C) effects were studied.

Experimental/methodology. The zirconium support was prepared by precipitation at pH 9 and the catalysts by incipient wetness impregnation. Phase α and β carbides were synthetised using a C_2H_4/H_2 25/75 mixture at 650°C, with a previous ammonia treatment for the α phase. The catalysts were caracterized by N2 physisorption, TPR-MS, DRX and XPS. Catalytic properties were studied in an agitated 25 mL batch reactor using water as solvent. The reactor was presurized with N_2 up to 6 bar and then heated to 250°C, reaching 46 bar. Reaction time was set at 90 min. Liquid products were analyzed by HPLC and gas products by gas chromatography (GC).

Results and discussion. Concerning catalytic performance, it was observed that ethanol conversion decreases with higher metal content (Figure 1a), which correlates with the carburization degree studied through TPR (Figure 1b). However, 10% Mo showed greater selectivity towards H_2, which might be explained by the oxicarbide presence detected through TPR (Figure 1b) and XPS. Reaction temperature has an effect on APR, being directly proportional to catalyst activity. H_2 production was favoured at 250°C. In addition, a higher ethanol conversion was observed for the α phase, in agreement with literature and which might be explained by a greater particle dispersion over the support. Nevertheless, H_2 selectivity was higher for the β phase.

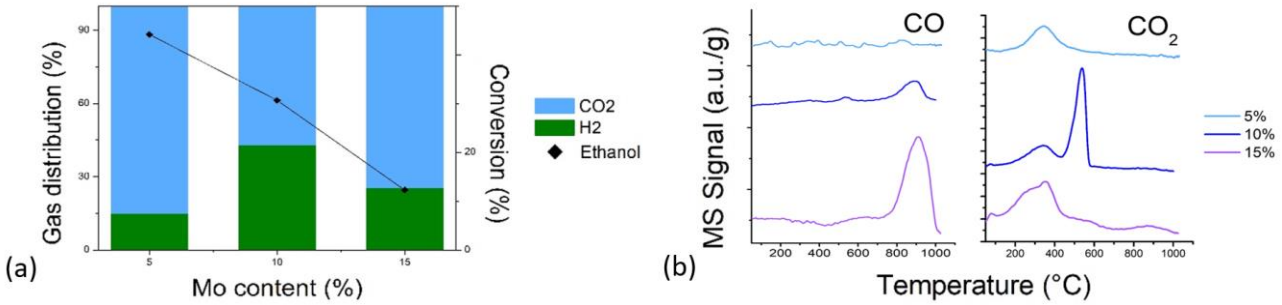

Figure 1: (a) Effect of Mo content on catalysts' activity and (b) MS-Signal for the TPR analysis.

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Inprovement of biocrude quality by HTL- catalytic assisted process

C. Moreira-Mendoza[1,2], S. Essounani[1], S. Molina-Ramírez[1], M. Cortés-Reyes[1], C. Herrera[1], M. A. Larrubia[1], L. J. Alemany[1*]

[1]*Departamento de Ingeniería Química. Facultad de Ciencias. Universidad de Málaga. Málaga. España*

[2]*Facultad de Ciencias Matemática, Física y Química. Universidad Técnica de Manabí. Ecuador*

e-mail: luijo@uma.es*

Keywords: biomass, biocrude

Introduction.

The growing demand for energy resources and the need to reduce the consumption of fossil fuels in favour of more sustainable processes have led to an interest in the production of biofuels trough different routes, such as gasification, pyrolysis or liquefaction of biomass. In particular, the HTL (hydrothermal liquefaction) process allows the obtaining of a high-oxigeneted biocrude through the thermochemical conversion of wet biomass. This contribution aims to produce a high quality Biocrude that can be use in refinery by an assisted catalytic liquefaction.

Experimental/methodology.

To compare the properties of the biocrude obtained and the performance of the process, five different biomasses were used, divided into two categories: higher lignin content (sugar cane bagasse, rice husk and pine nut husk) and lipid-rich (Yellow Horn seeds and *Scenedesmus Al*. microalgae). HTL-D tests were carried out for 40 min in a 600 cm^3 Parr 4842 stainless steel pressure stirred reactor operating under subcritical water conditions at 600 rpm and 280 °C. Catalytic assisted process (HTL-CA) was analyzed under the same conditions, adding a short-chain alcohol that acts as a hydrogen donor (glycerol 3 wt %) and a Ni-Pt/Al_2O_3 catalyst that induces the aqueous phase reforming (APR) [1] of the glycerol. The catalyst with 9 and 0.09 atoms per nm^2 of support of Ni and Pt, respectively. was synthesised using pellets of 6 mm in length and 4 mm in diameter. The composition of the biocrude obtained was analysed by (GC-MS), Perkin-Elmer 2400 equipment, and Parr 6050 calorimeter. Were used for elemental analysed (C, N, H, S, O) an HHV (Higher Heating Value) estimation, respectively.

Results and discussion.

The biocrude yield registered by HTL-CA increases with respect to the direct process with values of about 18 % for lignocellulosic biomasses and values between 60 and 70 % for lipid biomasses. A higher HHV, with values between 35 and 50 $MJ \cdot kg^{-1}$, and an increase in H/C ratio and a decrease in O/C molar ratio in comparison with the direct HTL process were observed.

The HTL-D produces the depolymerisation of the biomass and the incorporation of the glycerol in the presence of the Ni-Pt catalyst promotes the production of H_2 by APR which produces the hydrogenation, decarboxylation and decarbonylation of the biocrude, these reactions in tandem tend to the formation of more saturated hydrocarbons in which the main fraction was found between C6 and C10.

Acknowledgments

Authors want to thank the financial support of P20-00234-R Project. Plan Andaluz de Investigación, Desarrollo e Innovación (PAIDI 2020).

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Selective Hydrogenation with Ru Nanoparticles Immobilized on Aluminium Phosphate-Based Supported Ionic Liquid Phase Catalysts

W. Fang[†1], Y. Zhang[†2], A. Bordet[2*], A. Riisager[1*], W. Leitner[2]
[1]*Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, Kgs. Lyngby, Denmark*
[2]*Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany*
[†]*These authors contributed equally*
[*]*alexis.bordet@cec.mpg.de; ar@kemi.dtu.dk*

Introduction. Metal nanoparticles (NPs) synthesized from organometallic precursors on molecularly modified surfaces (NPs@MMS) show benefitial properties for the design of multifunctional catalysts [1]. Variations of the support, the molecular modifier, as well as the employed NP precursors enable the preparation of tailor-made catalysts [2-4]. NPs@MMS catalysts have been found to exhibit excellent selectivity control in the hydrogenation of biomass-derived furfuralacetone (FFA, **1**). The different functional groups in FFA (*i.e.*, C=O, C=C and furan ring) have different reactivity and the product distribution upond hydrogenation depends on both the reaction conditions as well as the nature of the catalyst (Figure 1a). In this work, a NPs@MMS catalyst composed of Ru NPs immobilized on an aluminium phosphate (APO-5) [4] support modified with ionic liquid (IL) (Ru@SILP) was introduced for FFA hydrogenation, and its reactivity compared to an analogous Ru@APO-5 catalyst without IL-modifyer and Ru@SiO_2.

Experimental/methodology. Modified APO-5 support (APO-5-OH) was prepared by hydrothermal synthesis followed by grafting with ionic liquids (when used) and introduction of Ru NPs *via* a wet impregnation method using an organometallic precursor.

Results and discussion. Ru@SILP(APO-5-OH) and three reference catalysts Ru@APO-5-OH, Ru@SILP(SiO_2), and Ru@SiO_2 were applied for the hydrogenation of FFA. The catalysts with the APO-5-OH support showed high selectivity for compound **3**, while the catalysts with SiO_2 support displayed high selectivity for compound **5** at 60 °C with 30 bar H_2 gas (Figure 1b), indicating that the adsorption mode of FFA might largely affect the product distribution. Furthermore, the selectivity of Ru@SILP(APO-5-OH) shifted from compound **2** to **3** and finally to **5** by increasing the reaction temperature from 20 to 200 °C (Figure 1c). Notably, the introduction of IL also made the Ru@SILP(APO-5-OH) more stable than the catalysts wihtout IL. In summary, the IL-modified APO-5-OH support generates a stable and highly durable Ru@MMS catalyst with temperature-controlled product selectivity for FFA hydrogenation and possibly also for alternative substrates with similar functionalities.

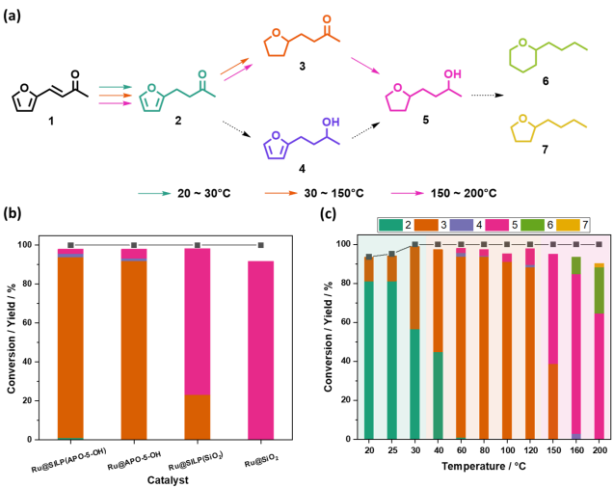

Figure 1. (a) Hydrogenation network of furfuralacetone; (b) Catalytic performance of different catalysts at 60 °C; (c) Catalytic performance of Ru@SILPs(APO-5-OH) at different reaction temperatures.

Acknowledgments
The authors acknowledge the Department of Chemistry, Technical University of Denmark and Max Planck Institute for Chemical Energy Conversion for support. W.F. acknowledges the China Scholarship Council for awarding a scholarship and Otto Mønsteds fond for a travel grant.

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Enhancing the bio-oil conversion using open cell foam structured catalytic reactors

E. Farah[1], E. Kantarelis[1, *]

[1] *KTH Royal Institute of Technology, Department of Chemical Engineering, Stockholm (Sweden)*
[*] *ekan@kth.se*

Keywords: open cell foam, structured reactors, process intensification, pyrolysis oil.

Introduction. A compelling step towards defossilizing current industrial processes is to replace fossil-based resources with biomass-derived ones. The catalytic upgrading of the biomass-derived oil, to produce important industrial feedstock such as light alkenes, emerges as an attracting alternative and takes place over microporous zeolites. Nevertheless, steric hindrances and diffusion limitations at particle scale combined with conventional packed bed reactor arrangement, that induces large pressure drop, temperature gradients, low external mass transfer and possibility of channeling [1], result in poor control of the mass (and heat) transfer at different scales promoting secondary reactions and altering the product distribution. Deposition of hierarchically ordered zeolite coatings on well-defined structures, such as open cell foams could enhance the overall mass transfer of the reactants to the active sites of the catalyst, control their reaction time, and thus improve conversion and selectivity to desired products [2-4].

In this study, the effect of different ZSM-5 coatings supported on an aluminum open cell foam catalyst on the catalytic cracking of biomass-derived oil is investigated. The catalytic performance and the deactivation behavior of the tested catalysts are compared to their activity in a packed bed configuration. More specifically selectivity to primary products (e.g., light olefins) and coke type and amount are of interest.

Experimental/methodology. Hierarchical ZSM-5 catalysts were prepared and coated on aluminum foam by hydrothermal treatment. The catalytic performance was evaluated at 600 °C and WHSV 1-7 h^{-1} and compared to runs using a fixed bed arrangement. The pyrolysis oil was injected in a pulse mode totaling 4 pulses of 15 mins each (Figure 1). The gas and liquid products were analyzed using gas chromatography.

Results and discussion. The conversion of bio-oil in a packed reactor revealed a fast decrease in the activity of the hydrothermally synthesized hierarchical HZSM-5 compared to the desilicated ones. The coke content (20%) was also higher than the Ds-HZSM-5 (14%) and the Fe-doped one (18%). The experiments using a foam supported catalyst are ongoing.

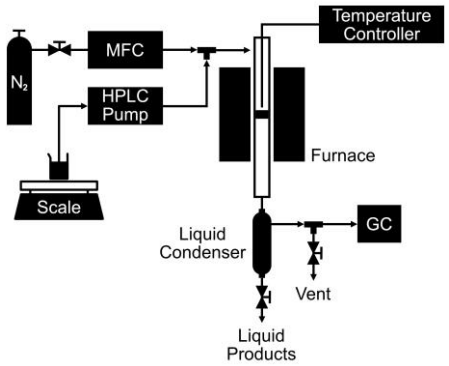

Figure 1 The experimental setup

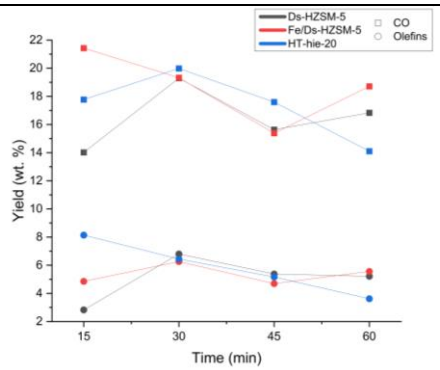

Figure 2 Olefins and CO yields of bio-oil conversion in a packed bed reactor. Ds-Desilicated ZSM-5; HT hie-nanosized hierarchical HZSM-5

Acknowledgments
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Direct production of 1,3-Butadiene from 1,3-Butanediol Dehydration

Ghinwa Fayad[1], Ekaterina Makshina[1], Loic Eloi[2,3], Bert Lagrain[1], An Verberckmoes[2], Bert Sels[1,*]

[1]*Center for Sustainable catalysis and Engineering, KU Leuven, Belgium*
[2]*Industrial Catalysis and Adsorption Technology, Ghent University, Belgium*
[3]*Laboratory for Chemical Technology, Ghent University, Belgium*
[*]*bert.sels@kuleuven.be*

Keywords: B-ZSM-5 zeolites, Direct dehydration, 1,3-Butanediol, 1,3-Butadiene

The most important and fundamental conjugated diene is 1,3-butadiene (BD), which is a key intermediate for the production of a variety of synthetic rubbers and polymeric resins [1]. Currently, over 98% of 1,3-BD is obtained as a by-product in ethylene plants during naphtha cracking or through the oxidative dehydrogenation of *n*-butane and *n*-butene [1,2]. However, the depletion of these non-renewable feedstocks increases the demand of BD production via greener and more sustainable routes based on bio-based renewable resources [3]. Butanediol isomers (BDOs) (such as 1,3-, 1,4- and 2,3-) can be produced in high yields from biomass by fermentation, therefore, the acid-catalyzed dehydration of such C_4 alcohols paves the way to alternative routes for bio-BD synthesis [3].

Our work aims to stably produce BD with a very high yield from the catalytic dehydration of 1,3-BDO in the gaseous phase. To realize this goal, the catalytic behaviour of several acidic commercial zeolites with different topologies were tested at 300°C under atmospheric pressure in a fixed-bed flow reactor. Results revealed that the framework structure of zeolites plays a crucial role in governing butadiene selectivity. In addition to topology, active site accessibility, acid strength and acid site density can have a prominent impact on conversion rate, selectivity as well as stability in such dehydration reactions. While better sites accessibility may lead to shorter diffusion paths in the catalyst particle and lower cokes formation, hence, higher conversion and higher butadiene selectivity may be achieved; weak acid sites might decrease propylene formation by hindering carbon-carbon catalytic cracking. To tackle these properties, new dehydration catalysts such as Boron-incorporated MFI zeolites were synthesized, and their catalytic activity was evaluated. The catalytic results of B-ZSM-5 compared to its proton analogous revealed the positive effect of Boron on the dehydration reaction. At a comparable Si/Al ratio, B-ZSM-5 displayed a superior activity and BD selectivity compared to the parent ZSM-5.

Acknowledgments
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Catalytic transfer hydrogenation of maleic acid to succinic acid on Pd/C catalysts using formic acid: a structure sensitive reaction

Victoria A. Francés[1*], A. Orozco-Saumell[1], P. Maireles-Torres[2], F. Vila[1], D. Martín Alonso[1], R. Mariscal[1], and M. López Granados[1]

[1]*EQS Group (Sustainable Energy and Chamistry Group), Institute of Catalysis and Petrochemistry (CSIC). C/Marie Curie 2, Campus Cantoblanco, 28049 Madrid, (Spain).,*

[2]*University of Málaga, Department of Inorganic Chemistry, Crystallography and Mineralogy. (Associated Unit to ICP-CSIC), Facultad de Ciencias, Campus de Teatinos, 29071 Málaga (Spain*

[*]*victoria.frances@csic.es*

Keywords: Succinic acid, Catalytic Transfer Hydrogenation, Pd/C, XPS, XRD, Rietveld analysis, TEM

Introduction. Succinic acid (SAc) and its dehydrated anhydride form, succinic anhydride (SA), which production mostly relies on the hydrogenation of maleic acid (MAc) or maleic anhydride (MA) derived from fossil oil, are used by the chemical industry in a number of applications, such as the production of 1,4-butanediol (BDO), γ-butyrolactone, pharmaceuticals, food and agrochemical products and in the production of polymers such as polybutylene succinate. A renewable route based on fermentation of sugars, currently at a demonstration level, presents several drawbacks associated with the separation and purification of SAc from the fermentation broth. This fossil route can become fully renewable if MAc is derived from biomass feedstock (like oxidation of furfural) and if it is hydrogenated with green H_2, like for instance that obtained from biomass-derived formic acid (FAc), that can also be obtained from biomass.[1]

Results and discussion. In this communication, we present our investigation to find an efficient catalytic technology to produce SAc from MAc in aqueous phase and using formic acid as a source of H_2 (the catalytic transfer hydrogenation (CTH) of MAc to SAc). Among all the catalysts tested, the catalyst system based on Pd particles supported on carbon (Pd/C) was found to be very active and selective for this reaction: neither extra organic solvents nor excess of FAc beyond the stoichiometric amount are needed. Besides SAc precipitates at the exit of the reactor which facilitates its separation. Interestingly the Pd/C system is very stable. Deactivation could only be detected when the WHSV of MAc was larger than 13 g MAc g cat^{-1} h^{-1}, but even at these conditions, the increase of the reaction temperature and/or the contact time (decreasing the flow rate) can mitigate the deactivation and still achieving very high SAc productivity. After 400 h on stream, the productivity was above 5300 g of SAc per g of catalyst.[1]

We also present the studies of the effect of the Pd particle size and of the type of C support (activated carbon, charcoal, mesoporous carbon, carbon nanotubes, graphene oxide, etc.) on the reaction rate. It was found that the reaction is sensitive to the structure. The intrinsic reaction rate of SAc formation increases with the particle size but for (average) diameter of particles size larger than 6 nm the intrinsic rate decreases (Fig 1).

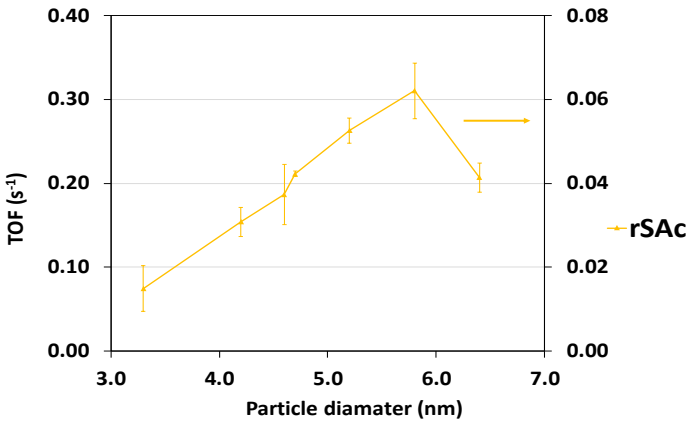

Fig 1. Intrinsic reaction rate of formation of SAc as a function of the Pd particle size

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Depolymerization of cellulose in lithium bromide solution promoted by heterogeneous acid catalysts

Mateus F. Paiva[1*], Robert Wojcieszak[1], Guillaume Vanhove[2], Fabio B. Noronha[1,3*]

[1]*Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – Unité de Catalyse et Chimie du Solide, Lille, France*
[2]*Univ. Lille, CNRS, UMR 8522 - Physicochimie des Processus de Combustion et de l'Atmosphère, Lille, France*
[3]*National Institute of Technology, Catalysis, Biocatalysis and Chemical Processes, Rio de Janeiro, Brazil.*
[*]*mateus.freitaspaiva.etu@univ-lille.fr*

Keywords: hydrolysis of cellulose, molten salt hydrate, solid acid catalysts

Introduction. A promising cellulose solvent is a highly concentrated aqueous solution of inorganic salts (molten salt hydrates – MSH) in the presence of inorganic acids, which can interact with the hydroxyl groups of cellulose, weakening and breaking the hydrogen bonds and then, leaving the β-(1-4) glycosidic units exposed and accessible to catalysts. However, these inorganic acids are highly corrosive, require steps of neutralization, and are not recyclable. In spite of their advantages, heterogeneous catalysts have not been used with MSH for cellulose depolymerization [1]. Hence, this study aimed to investigate the performance and stability of heterogeneous catalysts for cellulose one-pot solubilization and depolymerization, in lithium bromide (LiBr) reaction media.

Experimental/methodology. Four different commercial catalysts were used in this study: Ion-exchange polymer resin (Amberlyst-15, Sigma), modified sulfonated silica (SiliaBond®-PSA endcapped, Silicycle), zeolite (HZSM-5, Si/Al = 11.5, Zeolyst) and a metal oxide ($NbOPO_4$, CBMN). To measure the acidity of these catalysts, a titration with NaOH in aqueous phase was performed following a method described by Kim *et al.* [2]. Concerning hydrolysis studies, 50 mg of cellulose (Sigmacell Type 50, with a Dp = 1181) and 50 mg of catalyst were added to 2.5 g of LiBr solution (water/salt molar ratio = 3.25), in a reaction flask containing a stirring bar. The flask was sealed, heated to 90 °C and kept at this condition for 2 h, under stirring (600 rpm). Catalysts were separated and the resulting hydrolysates were analyzed by HPLC.

Results and discussion. The experiment without a catalyst produced only gluco oligomers (10%) and most of cellulose remained unreacted (90%). The addition of catalyst strongly decreased the yield of oligomers, which were converted into glucose, fructose, levoglucosan (LGA), HMF, and furfural, regardless of the catalyst (Table 1). Furthermore, the yield of glucose followed the order of total acidity of the catalysts and the nature of its acid sites. These results revealed that the Brønsted acid sites were responsible for the hydrolysis of gluco oligomers to glucose and its conversion to LGA and furfural, as well as, the dehydration of fructose to HMF. The Lewis acidity of the MSH performs the isomerization of glucose into fructose. Regarding the catalysts stability, it was observed a significant deactivation for the resin and the zeolite, while the metal oxide and the modified silica remained stable under the reaction conditions.

Table 1. Catalyts acidity and products distribution observed after hydrolysis screening on LiBr media.

Catalyst	Acidity (μmol g^{-1})	Products Yield (%)					
		Glucose	Gluco-oligomers	Fructose	Levoglucosan	HMF	Furfural
LiBr	-	-	10.0	-	-	-	-
Amberlyst-15	5223	50.9	43.2	-	0.70	3.40	0.80
SiliaBond-PSA	813	47.0	39.0	11.0	1.00	1.00	0.50
HZSM-5	668	42.5	46.0	10.0	1.30	-	-
$NbOPO_4$	538	39.0	47.0	10.4	0.80	1.60	0.30

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European Union's Horizon: 847568 - Pearl PhD Programme (I-SITE); Hauts-de-France Région, FEDER and MEL: CatBioInnov project; Programme Investissement d'Avenir (ANR-16-IDEX-0004).

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Aqueous phase hydrogenolysis of glycerol over Ni-Cu/Al catalysts with in-situ produced hydrogen

D. Gallego-García, M. Laria-Alonso, U. Iriarte-Velasco, M.A. Gutiérrez-Ortíz, J.L. Ayastuy*

Department of Chemical Engineering, University of the Basque Country UPV/EHU, Bilbao, Spain
**joseluis.ayastuy@ehu.eus*

Keywords: spinel, glycerol, aqueous phase, HDO, 1,2-propylene glycol.

Glycerol is an important candidate for the next-generation bio-feedstocks. It is an abundant coproduct in biodiesel production (around 10 wt.% of biodiesel) and a highly functionalized molecule so it can be transformed into an array of value-added chemicals. Generally, the glycerol hydrogenolysis involves the addition of H_2 from an external source, mainly produced from fossil resources. Glycerol, being an oxygenated molecule can undergo aqueous-phase reforming (APR) to generate hydrogen. Therefore, the use of hydrogen generated in-situ by APR would provide an alternative to external, high-pressure fossil-derived hydrogen and make the process safer and more sustainable [1]. Nevertheless, the objective to produce 1,2-propylene glycol by glycerol hydrogenolysis with H_2 generated by APR is quite challenging because of the design of bifunctional catalysts. These catalysts have to present the proper balance of metal and acid sites to reach a high selectivity toward 1,2-propylene glycol by using in-situ generated hydrogen.

In this work, a series of Ni-Cu aluminate spinels have been synthesized by one-pot sol-gel method, with a Ni/Cu molar ratio of 1/0, 0.95/0.05, 0.875/0.125, 0.75/0.25 and 0/1. For all the cases the Metal/Al=1/2 ratio has been kept. The synthesized solids have been characterized by different techniques to evaluate their metal and acid functions, textural properties, structure, morphology, reducibility, among others. Glycerol hydrogenolysis has been carried out in a fixed bed reactor at 235 °C and 45 bar (catalyst reduced in-situ at 800 °C, for 2 h) feeding a 10 wt.% glycerol/water solution and with a space velocity of 12 h^{-1}. The gas product of the reaction was analyzed by GC and the liquid product, at different reaction times, was analyzed by GC-FID and TOC.

Table 1. General properties of reduced catalysts.

Catalysts	d_{Metal} (nm)	S_{BET} (m^2/g_{cat})	DoR (800 °C)
NiAl	8.6	14	88.1
$Ni_{0.95}Cu_{0.05}Al$	9.2	57	81.8
$Ni_{0.875}Cu_{0.125}Al$	8.7	27	65.8
$Ni_{0.75}Cu_{0.25}Al$	9.5	58	37.1
CuAl	16.0	6	99.5

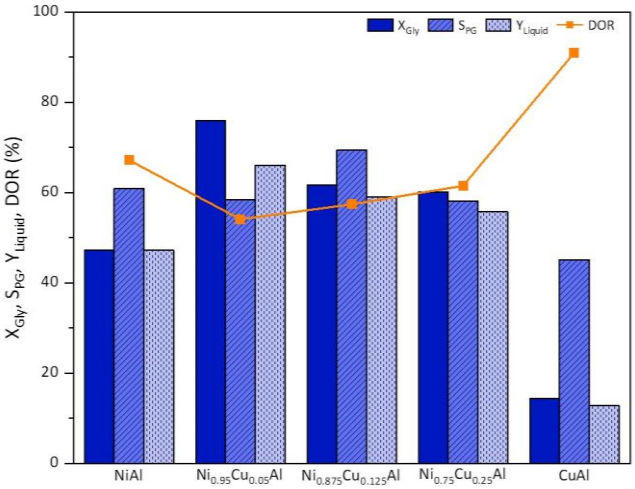

Figure 1. Glycerol conversion, Selectivity to Propylene Glycol, C-yield to liquids and Deoxygenation degree. Data at TOS (4 h).

Ni-containing spinel derived catalysts produced nanosized metallic particles upon reduction (< 10 nm). Also, bimetallic solids showed Ni-Cu alloy formation (XRD). Compared to monometallic solids, bimetallic reduced catalysts presented enhanced S_{BET}. The Degree of Reduction (DoR) of bimetallic solids decreased substantially upon Cu doping, due to the enhancement of the Cu-Ni-Al interaction. Therefore, less metallic Ni could be exsoluted from the spinel phase by reduction at 800 °C. The CuAl catalyst was not active to produce H_2 by APR; however, the presence of Ni enhanced H_2 production. Moreover, the H_2 generated by APR was consumed in-situ giving rise to HDO products, such as 1,2-PG. Bimetallic catalysts improved the reaction indices of the monometallic NiAl, being $Ni_{0.875}Cu_{0.125}Al$ catalyst the most selective to 1,2-propylene glycol.

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Acknowledgments

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Engineering the surface configuration of AgPd alloy catalysts for highly selective oxidation of 5-hydroxymethyl-furfural at room temperature

Yichao Jin[1], Huai-Yong Zhu[1*]

[1]*School of Chemistry and Physics, Queensland University of Technology, 2 George Street, Brisbane 4001, Australia*

[*]*hy.zhu@qut.edu.au*

Keywords: aerobic HMF oxidation, room temperature, bimetallic sites

Introduction. The production of 2,5-furandicarboxylic acid (FDCA) plays a pivotal role in chemical synthesis as it serves as a highly valuable and renewable platform chemical with diverse applications. FDCA is a key building block for the synthesis of bio-based polymers and materials, such as polyethylene furanoate (PEF), which offers a sustainable alternative to conventional plastics derived from fossil fuels. The selective oxidation of 5-hydroxymethyl-furfural (HMF) to FDCA is a promising pathway to efficiently obtain this valuable compound. However, achieving high selectivity/yield of FDCA at low temperatures is challenging with the currently available catalysts. To address this challenge, our research proposed both thermalcatalysis and photocatalysis systems using AgPd alloy NPs supported on CeO_2.

Experimental/methodology. A 20 mL Pyrex glass tube was used as a reaction container. The reactants and catalyst were added, and the tube was sealed with a rubber septum cap under the O_2 atmosphere. The reaction mixture was stirred using a magnetic stirrer while keeping a temperature of 20 °C. The filtered samples were analyzed using high-performance liquid chromatography (HPLC) and an LTQ Orbitrap Elite mass spectrometer at a temperature of 30 °C.

Results and discussion. The $Ag_{1.5}Pd_{1.5}/CeO_2$ catalyst exhibited a remarkably high yield of FDCA at 20°C, making it a promising method for room temperature production of FDCA from sustainable sources. Both the experimental results and DFT simulations indicate that the selective oxidation process is strongly influenced by the appropriate chemisorption strength of reactants, intermediates, and products on the metal NPs. Adjusting the Ag/Pd ratio allows for finely tuning the surface configuration to modify its adsorption capabilities. The bimetallic boundary sites of $Ag_{1.5}Pd_{1.5}$ NPs exhibit a moderate adsorption capacity for reactants and intermediates, surpassing the activation energy barriers involved in the oxidation of carbonyl and alcohol groups, while efficiently avoiding side reactions. The scale-up results demonstrated a remarkable FDCA yield at the 100g level, indicating the significant potential of this catalyst for industrial applications. Our recent exploration involves designing a low Pd content AgPd photocatalyst, achieving an FDCA yield exceeding 99% under low-flux light illumination. The results provide an alternative approach for sustainable and environmentally friendly production of FDCA.

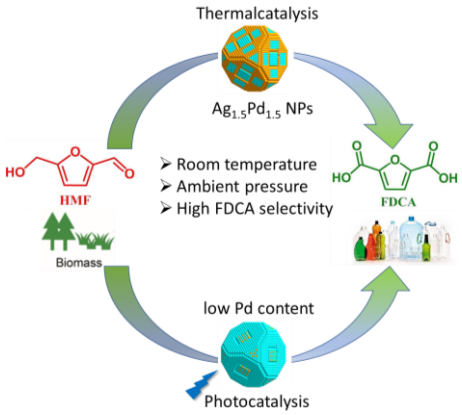

Figure 1. Scheme of thermal catalysis and photocatalysis process of selective HMF oxidation using AgPd alloy catalysts.

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Hydrogen-driven Deoxydehydration of Vicinal Diol Compounds over Anatase-titania-supported Molybdate-Copper Catalyst

J.X. Gan[1], Y. Nakagawa[1,*], M. Yabushita[1], K. Tomishige[1,*]

[1]*Department of Applied Chemistry, School of Engineering, Tohoku University, Sendai, Japan*

[*]*yoshinao@erec.che.tohoku.ac.jp; tomishige@tohoku.ac.jp*

Keywords: deoxydehydration, biomass-based platform chamicals, selectively reduction

Introduction. Biomass-based platform chamicals such as sugar alcohols are highly oxygened, and deoxydehydration (DODH) reaction is useful which converts vicinal diols into corresponding alkenes in one step (**Fig. 1**). In pervious study[1], Re-based catalysts such as ReO_x-Au/CeO_2 achieved high yield in DODH reaction. Meanwhile, application of noble metal based catalysts is limited by the high cost. Therefore, the development of new DODH catalysts that do not contain noble metals was targeted in this research. We have recently reported MoO_x-Au/TiO_2 catalyst for DODH reaction[2]. To further decrease the cost of this catalysts, non-noble additive metal instead of Au was explored (Fe, Co, Ni, Cu) for MoO_x/TiO_2 (anatase) catalysts.

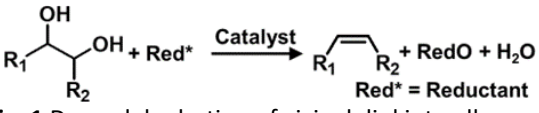

Fig. 1 Deoxydehydration of vicinal diol into alkene.

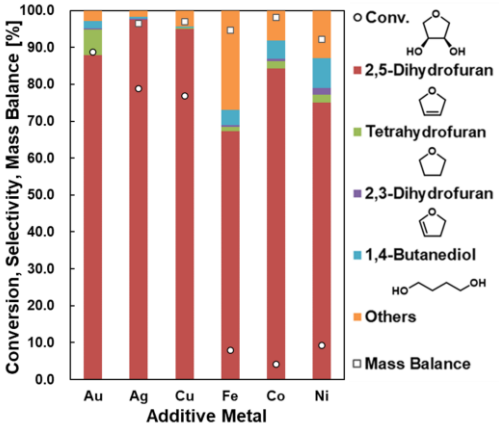

Fig. 2 Effect of additive metal (M) on the catalysis of MoO_x-M/TiO_2 (anatase) for DODH of 1,4-anhydroerythritol. Condition: MoO_x-M/TiO_2 (Anatase) (Mo: 1 wt%, M: 2 wt%) 0.15 g, 1,4-anhydroerythritol 0.5 g, 1,2-dimethoxyethane 4 g, 463 K, H_2 8 MPa, 4 h.

Experimental/methodology. Sequential impregnation method was used in preparation of catalysts with uncalcined TiO_2 (anatase), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (AHM) and metal nitrates as support, Mo precursor and additive metal percurosr, respectively. Autoclave with an inner glass vessel was used as reactor. The products were analyzed with by GC-FID.

Results and discussion. The effect of additive metal (M) is summerized in **Fig. 2**. Cu showed the highest conversion and selectivity to the DODH product among first-row transition metals as additives. In the activity test with various loading amounts of Cu and Mo, the catalyst with 2 wt% Cu and 1 wt% Mo showed the highest conversion up to 78.8% with selectivity of 98.2% to DODH product in the condition of 463 K and 4 h. However, after 8 hours in the time course experiment, the catalyst began to produce by-product (1,4-butanediol). Referring to earlier research[3], the carbonaceous species accumulated on the catalyst can promote the conversion of 2,5-dihydrofuran to 1,4-butandiol. Acidity of catalyst can be responsible to the formation of carbonaceous species. To increase the selectivity of DODH product, basic Mo precursor ($NaMoO_4$) was added in the catalyst preparation process. As a result, the selectivity of 24 h reaction was successfully increased to 88.6% from 36.4% obtained with single AHM as precursor (**Fig. 3**). The Mo precursor weight ratio of 9:1 showed the best conversion and selectivity in activity tests using various ratio of Mo precursors. Additionally, the MoO_x-Cu/TiO_2 (anatase, mixed Mo precursor) catalyst was stable for at least 4 uses according to the reusability test. The reaction order was around 0.1 with respect to both the substrate concentration and the H_2 pressure which suggests that the extrusion of the alkene is the rate-determining step. Besides, XAS and TEM tests were performed to characterize the catalysts.

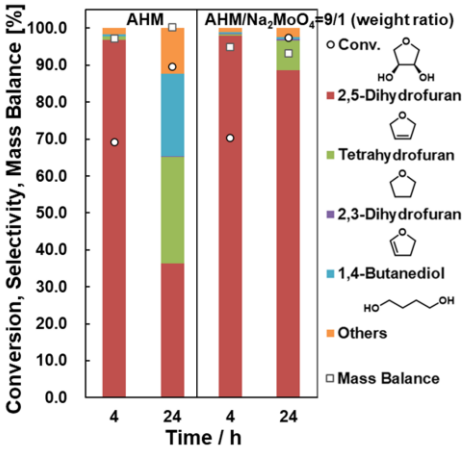

Fig. 3 Effect of Mo precursor on the catalysis of MoO_x-Cu/TiO_2 (anatase) Condition: MoO_x-Cu/TiO_2 (anatase) (Mo: 1 wt%, Cu: 2 wt%) 0.15 g, 1,4-anhydroerythritol 0.5 g, 1,2-dimethoxyethane 4 g, 463 K, H_2 8 MPa.

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This work was supported by KAKENHI 18H05247 and 20H02519.

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Zeolite catalysts for the (bio)ethanol to (bio)hydrocarbons process

G.Busca[1*], E.Spennati[1], E.Finocchio[1], P.Riani[2], G.Garbarino[1]

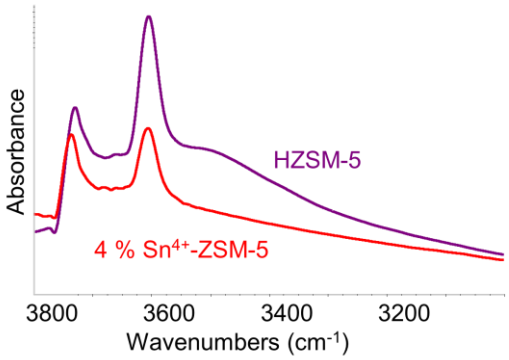
[1*]*Department of Civil, Chemical and Environmental Engineering, University of Genoa, Genoa, Italy*
[2]*Department of Chemistry and Industrial Chemistry, University of Genoa, Genoa, Italy*

Keywords: zeolite; tin; zinc; biohydrocarbons.

Introduction. The production of hydrocarbons, such as e.g. olefins [1] and aromatics [2], from renewable sources will likely be of interest in the near future, to produce sustainable fuels and to manufacture sustainable intermediate chemicals for the chemical industry. Bioethanol, either produced by fermentation of ligneocellulosic matter or algae [4], by CO_2 hydrogenation with green hydrogen [3], or even by fermentation of biosyngas [5], according to its low toxicity and limited volatility, is an interesting intermediate. The conversion of ethanol to hydrocarbons using zeolite catalysts was proposed years ago [6], and is of renewed interest today [7,8]. In the present communication a study of protonic and of tin, zinc and iron based ZSM5 zeolite for the ethanol-to-hydrocarbon processes is proposed.

Experimental/methodology. Zeolyst (CBV 5524 G) NH_4-ZSM5 was used as the starting material for catalyst preparation, including parent zeolite. Cationically exchanged ZSM5 zeolite catalysts (1 and 4 wt. % of Fe^{3+}, Zn^{2+}, Sn^{2+}, Sn^{4+}, and, a 1:1 wt ratio, 2 wt.% Zn^{2+}-Sn^{2+} bimetallic sample) have been prepared by incipient wetness impregnation technique from Fe and Zn nitrates and Sn chlorides, followed by calcination in air at 773 K for 4 h. Characterization was realized using X-Ray Diffraction, UV-vis-NIR and skeletal FT-IR spectroscopies. Surface characterization and surface activity tests were realized by FT-IR spectroscopy with a home-made gas adsorption and reaction cell. Steady state catalytic activity was investigated with a fixed bed flow microreactor with 0.5 $g_{catalyst}$, 170 cc/min of 2.4 vol.% ethanol/nitrogen mixture. Product analysis was realized by GC and GC-MS. TPSR experiments were also realized with continuous on-line IR analysis.

Results and discussion. For all investigated catalysts, in steady state conditions, diethylether is the main reaction product at T ≤ 473 K when conversion is still incomplete. On the other side, in most cases, ethylene yield approaches 100% at around 523 K. Higher hydrocarbons yield grows up to a maximum in the range 623-723 K, and most frequently decreases at higher temperature with reincrease of ethylene yield. 1 wt% tin-impregnated zeolites and the protonic form appear to be the most active in the production of hydrocarbons C_{3+}. Maximum yield to C_{3+} hydrocarbons is 70 % observed at 673 K on 1 wt% Sn^{4+}-impregnated ZSM5 zeolite and 67% at 673 K on the protonic form. Maximum propylene yield is observed at 723 K over the protonic form, 35 % and on 1% Sn^{4+} impregnated zeolite, 30 %. Maximum C_4 yield (32%) is observed at 623 K on 1% Sn^{2+}-impregnated zeolite. 1% Sn^{2+} and Sn^{4+} impregnated zeolites are also the best catalysts for the production of "biogasoline" (C_{5+}), up to 30 % yield, and of C_{6+} hydrocarbons, including aromatics. Characterization results, in particular those arising from IR spectroscopy of adsorbed species, allow us to discuss the catalytic data in terms of activity of residual Brønsted acid sites (see the figure) and Lewis acidity of the impregnated cations.



FT-IR spectra of the surface -OH groups of zeolite catalysts

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Sequential Hydrogenolysis and Guerbet Reaction of Bio-carboxylic Acids to Plasticizer Alcohols (C8-C12) over Dual-Functional Heterogeneous Catalysts

Mahlet N. Gebresillase [1a], Jeong Gil Seo [a]*

[a] *Department of Chemical Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 04763, Republic of Korea*

[*] *Corresponding author: jgseo@hanyang.ac.kr*

Keywords: Bio-carboxylic acid Hydrogenolysis, Guerbet reaction, Plasticizer alcohol,

Introduction: Plasticizers are low-volatility liquid or solid substances that are added additives to increase the flexibility or workability of materials[1]. Almost all plasticizers are synthesized from acids and alcohols[2]. Plasticizer alcohols are primarily synthesized from Alkenes via hydroformylation to aldehydes, followed by aldol condensation and hydrogenation[3]. Given the environmental issues associated with fossil fuel feedstock, developing new methods for efficiently synthesizing plasticizer alcohols from renewable biomass sources is crucial.

Experimental/methodology : Ru-based monometallic and bimetallic catalysts supported on SBA-15 were synthesized using a one-pot co-precipitation method for the catalytic hydrogenolysis of butyric acid, and hexanoic acid conducted using a high-pressure continuous reaction system. The guerbet reaction was performed in a Parr batch reactor over Ni-MgAl-LDH catalyst. After the catalyst was filtered out, liquid products were analyzed using liquid chromatography (HPLC).

Results and discussion: The continuous high-pressure reaction proceeds via the hydrogenolysis of butyric/ hexanoic acid to the intermediate aldehyde, followed by the subsequent hydrogenation of the aldehyde to alcohol. The obtained alcohol is subjected to Guerbet reaction where the *in situ* coupling over MgAl and hydrogenation over Ni to attain C8 and C12 plasticizer alcohols are completed. Butyl butanoate and Hexyl hexanoate are formed in trace amounts from the esterification of butyric acid, butanol, hexanoic acid, and hexanol, respectively, catalyzed by the SnO_x and the SBA-15. Ru/SBA-15 exhibits low activity due to the difference in the reactant adsorption sites (Ru). Ru_3Sn_7 alloy was the active center for hydrogenation. SnO_x was determined as an adsorption site for C=O because of its positive charge (acidity), whereas Ru bonds with Cα and provides hydrogen transfer. The association between catalyst properties and reaction pathway and yield was further studied. It was possible to obtain a yield of up to 86% C8 and 74% C12 plasticizer alcohols directly from butyric acid and hexanoic acid, respectively.

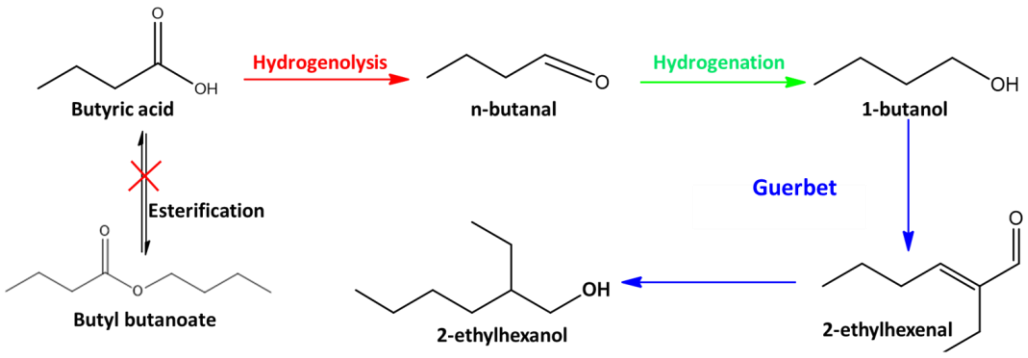

Figure 1: Reaction scheme for the synthesis of plasticizer alcohol from bio-carboxylic acid.

Acknowledgments

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Assessing acid – base cooperativity of layered oxides for biomass conversion

L. Giloni,[1] B. Cohen,[2] D. shpasser,[1] E. Gross,[2] and O. Gazit[*1]

[1]*Technion - Israel Institute of Technology, Haifa, Israel*
[2]*Hebrew university, Jerusalem, Israel*
[*]*Ozg@technion.ac.il*

Introduction. Aldol condensation of biomass derived molecules is highly attractive for the upgrading of biomass to value added chemicals. While Aldol condensation can be promoted by acid or a base catalysts efficient acid-base cooperative interactions can facilitate lower activation barrier, lower reaction temperature, and better control over reaction selectivity. $MgAlO_x$ based Layer double hydroxides (LDH) act as a base catalyst for aldol condensation. If the LDH is deposited as thin (order of 1 nm) layers on the surface of an acidic metal oxide the material can have acid-base properties at the interface between the two oxides. In the current work, we study the acid-base functionalities of MgAlOx thin particles deposited on an underlying support (i.e., ZrO_2). The catalysts are tested for the Henry reaction as a model reaction and the condensation of Furfural with Cyclohexanone.

Experimental/methodology. The catalyst was prepared through the synthesis of LDH thin sheets according to Leib, E. W. *et al.*[1] and depositing them on either commercial oxides or dedicated zirconia and yttrium doped zirconium (YSZ) were prepared based on the protocol of Yu et al.[2] Reaction testing was performed on a particulate catalyst while single particle characterization was performed by depositing the LDH thin particles on a zirconia coated Si-wafer. Reaction testing are performed in a batch mode and were analysed using ^{1}H-NMR and GC-MS.

Results and discussion. Following catalyst preparation, we compared the performance of the calcined hierarchical catalyst (LDH/ZrO_2, HOX) to that of the calcined native LDH (LDO) and ZrO_2 oxides and their mechanical mixture in the Henry reaction, **Figure 1**. We find that the LDO (layered double oxide) is the most active with 0.032 mol/mg_{cat}, the ZrO_2 is the least active with 0.002 mol/mg_{cat} and the mechanical mixture of LDO and ZrO_2 is 0.003 mol/mg_{cat}. The HOX catalyst per gram catalyst was slightly more active with 0.008 mol/mg_{cat}. However, normalizing the conversion levels to the amount of LDO in each sample we find that the HOX out performed the LDO by almost 20-fold, **Figure 2**. This difference cannot be explained by surface area as the ZrO_2 and HOX have roughly 10 m^2/g and the LDO is about 140 m^2/g. Hence, as the ZrO_2 is almost inactive the higher activity of the HOX and mechanical mixture is postulated to originate from specific active sites generated at the interface between LDO and ZrO_2. To better understand this effect we performed kinetic analysis, acid/base chemisorption at the macroscopic level and at the single particle level using AFM-IR. Work on the aldol reaction is in progress as well as additional analytical characterizations.

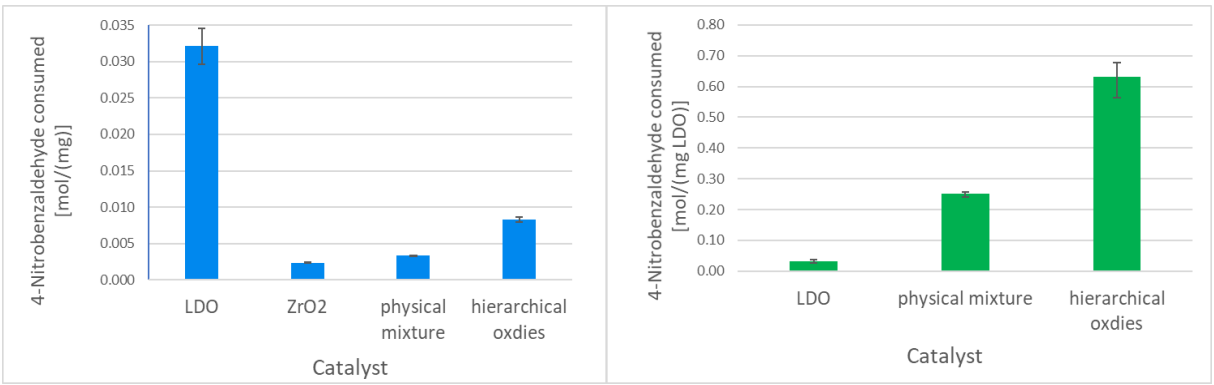

Figure 1(left) Conversion per mg catalyst of Nitroaldol condensation reaction @15h at 80C
Figure 2(right) Conversion per mg LDO of Nitroaldol condensation reaction @15h at 80C

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Ni/Al_2O_3-ZrO_2 catalyst for co-pyrolysis of lignocellulosic biomass and waste plastic to hydrogen-rich gas

Marcin Jędrzejczyk[1], Aleksandra Podlaska[1], Jacek Grams[1*]

[1]*Institute of General and Ecological Chemistry, Faculty of Chemistry, Lodz University of Technology Lodz, Poland*
[*]*jacek.grams@p.lodz.pl*

Keywords: nickel, zirconia, alumina, co-pyrolysis, lignocellulosic biomass, waste, polymers, hydrogen

Introduction.
The problem of waste disposal and the need to become independent of fossil fuels encourages researchers to develop new methods of the production of renewable energy. Thermal conversion of lignocellulosic biomass and waste plactic turns out to be one of the most promising among them [1]. Simultaneous use of both types of feedstock results in the increase in the production of valuable products (including hydrogen), which is related with synergic effect between lignocellulose and polymer. Unfortunately, the efficiency of the mentioned process is still unsatisfactory. The yield of produced hydrogen can be improved by the use of catalysts [2]. However, their catalytic performance can be limited due to carbon deposition or thermal instability [3]. Therefore, the main goal of this study was to develop active and stable catalyst for co-pyrolysis of lignocellulosic biomass and waste plastic to hydrogen-rich gas.

Experimental/methodology.
In the first step mixed Al_2O_3-ZrO_2 supports with various alumina content were synthesized. Then nickel was deposited on their surface by impregnation method. For comparison Ni/Al_2O_3 and Ni/ZrO_2 were prepared. Catalytic activity tests were conducted under atmospheric pressure at 700°C with the use of cellulose, real biomass samples and waste polymers. Co-pyrolysis was performed in a two step fixed bed quartz reactor. The feedstock was decomposed at 500°C. Then, formed pyrolysis intermediates were upgraded in catalyst bed at 700°C. The gaseous products were analyzed by gas chromatograph equipped with TCD detector. Physicochemical properties of prepared catalysts were characterized using TPR, TPD-NH_3, TPD-CO_2, XRD, ToF-SIMS, FTIR and microscopic techniques. TG-DTA was used for the evaluation of coking rate and catalyst stability.

Results and discussion.
The obtained results showed that both selectivity and activity of Ni catalysts depends strongly on the composition of support. Preliminary results showed that nickel supported on mixed Al_2O_3-ZrO_2 (with the ratio 1:1) allowed for the most efficient production of hydrogen. The catalytic performance of the studied materials was affected by porosity, acidity, crystallographic structure of support and reducibility of active phase, among others. Al_2O_3 possessing higher number of acid sites showed promising activity, but at the same time, was more susceptible to progressive deactivation due to coke deposition. The addition of ZrO_2 lowered acidity, but increased resistance against carbon deposit formation and catalyst stability. It can be related to its redox properties and higher oxygen storage capacity. Moreover, zirconia is able to adsorb water molecules present in the reaction mixture and facilitate their decomposition. This may result in the formation of hydroxyl groups on the catalyst surface participating in gasification of deposited carbon [4].

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Arabinose oxidation on Gold Based Extrudates Catalyst

Mouad Hachhach [1,*], Irina Simakova [2], Kari Eränen [1], Dmitry Murzin [1], Tapio Salmi [1]

[1] *Åbo Akademi, Johan Gadolin Process Chemistry Centre (PCC), Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku/Åbo Finland*
[2] *Boreskov Institute of Catalysis, Novosibirsk 630090, Russia*
[*] *Mouad.hachhach@abo.fi*

Keywords: Oxidation, Arabinose, Gold catalyst, Extrudates.

Introduction. Catalytic oxidation of monomeric sugars extracted from hemicelluloses appearing is biomass is regarded as an attractive way to valorise biomass. Hemicelluloses can be easily hydrolysed to sugar monomers and oligomers, which can be converted to valuable products. From this perspective, the catalytic oxidation of arabinose sugar which is present in large amount in the hemicellulose arabinogalactan is studied, focusing on the effect of liquid flow rate on the arabinose conversion.

Experimental/methodology. Gold on alumina (3%) catalyst extrudates were used in the experiments. The catalyst was reused for all the performed experiments. The experimental device was a combination of a packed bed reactor, a pH controller to ensure a constant pH, a recycling tank and a recycling pump. The first set of experiments was performed using a recycling flow of 200ml/min, then the second one using the 250ml/min and the last one 150 ml/min flows. Some experimental results are collected in Figure 1. The results show that for all the flows have a high conversion rate (95% for the 150 ml/min flow and 99% for the other ones) was reached fpr all the front rates. However, it is also observed that the higher the flow rate the conversion rate is slightly higher.

Results and discussion.

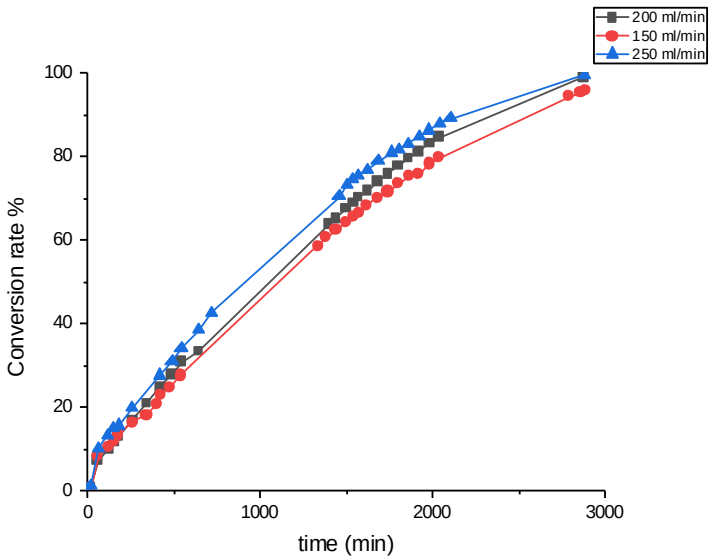

Figure 1: Conversion rate of arabinose to arabinonic acid at various liquid flow rates in recycled packed bed.

The results revealed that the flow rate has a slight impact on the arabinose conversion, which can be attributed to the fact that since the reactor system is a closed one, so the contact time between reactants and catalyst can be proportional to the liquid phase flow which increased the conversion of arabinose and even suppressed the external mass transfer resistance around the catalyst extrudates.

Acknowledgments
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Mixed oxides as heterogenous catalyst for transesterification and Guerbet reaction

Martin Hájek*[1], Karel Frolich[1], Jaroslav Kocík[2], David Kocián[1], Jan Malina[1]

[1]*University of Pardubice, Faculty of Chemical Technology (department of Physical Chemistry), Studentská 573, 532 10 Pardubice, Pardubice, Czech Republic*
[2]*ORLEN UniCRE, Inc., Areál Chempark 2838, 436 70, Litvínov-Záluží 1, Ústí nad Labem, Czech Republic*
**martin.hajek@upce.cz*

Keywords
Mixed metal oxides, Guerbet reaction, alcohols, transesterification

Introduction
The metal mixed oxides are acid-base catalysts used for many reactions such as transesterification (ester formation), Guerbet reaction (higher alcohol formation) or aldol condensation, i.e., preparation of fuels or chemicals from biomass. The non-edible *Camelina sativa* oil (second generation) was used for transesterification.

The mixed oxides were prepared by heating of double layer hydroxides to the temperature of 450 °C. The formula of hydrotalcite is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}A^{n-}_{x/n}\cdot zH_2O$, where *M* represents bivalent (Mg, Ca and Zn) or trivalent metallic cations (Al and Fe), A^{n-} is an anion (inorganic or organic) and *x* is the stoichiometric coefficient of M^{3+}. The type and molar ratio of metallic cation and the way of synthesis influence the properties and structure of formed hydrotalcite. The catalyst activity is also influenced by impurities remaining in hydrotalcites, especially sodium ions.

Experimental
For the transesterification, the Mg-Al hydrotalcites (constant molar ratio Mg to Al 3:1) were prepared by the coprecipitation method from nitrates of aluminum and magnesium with various types of anions. The transesterification was carried out at different weight hour space velocities and different reaction temperatures, with tested every parameter for 32 h. Moreover, the stability of the catalysts was tested by the determination of the metal content in the reaction mixture.

The Guerbet reaction was catalysed by Mg-Al mixed oxides (i) pure and (ii) with addition of transition metals such as Co, Ni, Cu, Mn and Cr (synthesized by coprecipitation). The transition metals were added to increase the redox properties. The catalytic synthesis of butanol from ethanol proceeded in a microflow reactor at a constant weight hour space velocity (4.5 h^{-1}) and different reaction temperatures (280, 300 and 350 °C). Other products, such as ethylene, 1,1-diethoxyethane, ethyl acetate, 1-hexanol, etc. were also determined and the reaction pathway for their formation was examined.

The synthesized materials (hydrotalcites and mixed oxides) were characterized by several experimental techniques such as XRD, TG-MS, TPD-CO_2, DRIFT and SEM.

Results and discussion
The presentation will introduce and compare the use of Mg-Al mixed oxides as heterogeneous catalyst for (i) the transesterification of non-edible *Camelina sativa* oil and (ii) ethanol conversion to higher alcohols such as butanol, hexanol (Guerbet reaction). It was found, that sodium impurities were bonded predominantly in the form of sodium nitrates (nitrates were used for hydrotalcite synthesis). The sodium influenced especially acid-base properties and so the ester yield, because the sodium nitrates blocked the pores and also disturbed the TPD determination. For Guerbet reaction, the relationship between structure, activity and stability was described. It was found that the presence of nickel, copper and cobalt positively influenced the catalyst activity. Moreover, some results were statistically evaluated.

Acknowledgments
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Efficient Heterogenous Sonocatalysis by Porous Heteroatom-doped Carbons in Selective Oxidation and C-C Coupling of Syringic Alcohol

Behdokht Hashemi Hosseini*[a], Dariusz Lomot [a], Rafael L. Oliveira [b] , and Juan C. Colmenares[a]

[a]*Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland*

[b] *Instituteof Low Temperature and Research Structure of the Polish Academyof Sciences*

Bhashemi.hosseini@ichf.edu.pl, jcarloscolmenares@ichf.edu.pl

Keywords: Sonocatalysis, Carbon-based materials, Selective oxidation, Catalysis, Porous materials, C-C reductive coupling, Biomass valorization

Introduction.

Sonocatalysis is one of the most important and effective advanced oxidation processes for destruction and mineralization refers to the chemical process realized by passing ultrasonic waves through liquid environments [1,2]. Focusing on sonocatalytic valorization of lignocellulosic biomass and their platform molecules by carbonaceous materials can be regarded as a key route enabling technology for pretreatment and conversion of lignocellulosic biomass [3]. The unique physicochemical properties and abundancy of carbon-based materials lead us to use the porous carbon materials doped with N, P, or B in our research for sonocatalysis which is rarely reported compared to traditional carbons [1,4]. It is worthy to mention that the alternation in the substrate from benzyl alcohol in other studies to syringic alcohol and assesment of the selective oxidation and C-C coupling of mentioned substrate is also the matter of concern in this study.

Experimental/methodology.

In the current investigation, the sonocatalytic activities were studied for the selective oxidation and C-C coupling of syringic alcohol. Various frequencies (22 kHz, 100kHz, 340 kHz, 500 kHz, and 800 kHz) were *used for evaluating the sonocatalytic activity of the four carbon-based catalyst namely C-meso, Chit-1, CN*-800-3, and C6-800-W [1]. After sonocatalytic tests in batch system, the collected samples were analyzed by *HPLC and reported as conversion, selectivity, and yield for favorable products which were syringaldehyde* and syringic acid. Finally, the best catalyst was chosen as sonocatalytic-active carbon material.

Result and Discussion

Properties of C-meso, as the best sonocatalytic-active catalyst, were examinated by N_2 sorption which showed the high specific surface area (more than 800 m^2/g). In the XRD pattern, all heteroatom-doped mesoporous carbons show two broad reflections at around 25°C and 43.5°C,which can be assigned to the (002) and (100) lattice planes [1]. After sonocatalytic tests, the conversion of 73% and selectivity to synergaldehyde was 40%. The Raman spectra show the defective structure and graphitic sites. The D-band results from the imperfect sites in sp2 carbon lattice such as edges/vacancies, topological defects, functionalities, and the presence of heteroatoms. The control reactions were performed by normal stirring on all porous carbon materials and the only sonocatalytic active catalysts was C-meso that has different selectivity for aldehyde while using lower frequencies and in higher ones toward acid. The morphological features of C-meso are investigated by TEM. SEM analysis shows that the materials present a non-uniform particle size and morphology; however, the chemical mapping (EDS) shows a homogeneous distribution of heteroatoms throughout the particles.

Acknowledgments

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Ruthenium Catalysts for the Efficient Conversion of 5-HMF into DFF to Produce Phenolic Resins

Franziska Heck[1*], Ingo Gräf[1], Hendrik Spod[1], Christoph Derflinger[2] and Birgit Kamm[2]
[1]*Heraeus Deutschland GmbH & Co. KG, Hanau, Germany*
[2]*Wood K plus, Kompetenzzentrum Holz GmbH, Linz, Austria*
**franziska.heck@heraeus.com*

Introduction. The negative impacts of global warming and greenhouse gasses, including the CO_2 emission, are widely recognized by society, politics, academia, and industry as complex challenges. [1-3] To move away from the dependence on petroleum-based chemistry, the cooperation program "Competence Centers for Excellent Technologies (Comet)" focuses on the valorization of organic materials and the total biomass utilization into sustainable products and energy. The native biopolymers from woody biomass are separated to obtain 5-hydroxymethyl (5-HMF) as starting material for bio-based products. In this paper, we highlight the development of an efficient oxidation of 5-HMF into 2,5-Diformylfuran (DFF) using new Ruthenium-based catalysts to produce biobased formaldehyde free phenolic resins from biomass. [4, 5]. Also, the attractiveness of precious metal (PM) catalysts, when applying recycling strategies, are presented.

Experimental/methodology. For the investigations, different ruthenium-based catalysts were synthesized. In a 450 mL stainless-steel autoclave (Parr Instrument Company), HMF (500 mg) was dissolved in 100 mL solvent (toluene, ethanol, *n*-hexane). After adding the catalyst Ru/Al_2O_3 (500 mg), the suspension was stirred vigorously (300 rpm) at RT while purging with molecular oxygen (flow rate 100 mLmin-1) for 10 min. After the reaction temperature was reached, the desired oxygen pressure was set via a gas inlet valve. The samples were analyzed with an Agilent 1100 series HPLC connected to a UV-vis detector, an AminexR HPX 87P column (300×7.8 mm, 9 µm particle size) and aqueous sulfuric acid (5 mM) as the mobile phase at of 298 K (flow rate 0.6 mLmin-1, injection volume 10 µL). The concentrations of HMF, DFF, FFCA, HMFCA, and FDCA were determined by external calibration at a detection wavelength of 280 nm.

Results and discussion. We developed the heterogeneous catalytic oxidation of 5-HMF with molecular oxygen for the efficient formation of DFF using new Ruthenium-based catalysts. The catalyst performance depends not only on the used solvent, but also strongly on the PM precursors, e.g., Ruthenium chloride or Ruthenium nitrosyl nitrate, and on the intrinsic support characteristics. To investigate the support influence, different $3\%Ru/Al_2O_3$ catalysts were synthesized on different alumina and were tested. It is noteworthy, that no 5-formyl-2-furancarboxylic acid (FFCA), 5-hydroxyme-thyl-2-furancarboxylic acid (HMFCA) or 2,5-furandicarboxylic acid (FDCA) were detected as over-oxidation products with none of our catalysts. After washing, the Ru/Al_2O_3 catalyst can be reused several times. Nevertheless, after the catalyst is deactivated, the PM recovery plays a key role from both an ecological and economical point of view. The full "PM loop" consists of the PM winning, PM solution production as well as the catalyst synthesis, followed by the performance as active catalyst. Finally, the deactivated catalyst is separated from the reaction mixture to close the loop with the PM recycling. The recycled secondary PM can reduce the carbon footprint up to 98% in comparison to primary PM from mining.

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Hydrogenation of furfural on pure and substituted perovskites as precursor catalysts

K. Lara, G. Pecchi[1,2], C. Sepúlveda[1,2], C. Herrera[1,2*]

[1]*Depto Físico-Química, Fac Cs Químicas, Universidad de Concepción, Chile*
[2] *Millennium Nuclei on Catalytic Process towards Sustainable Chemistry (CSC), Chile*
[*]*carlaherrerah@udec.cl*

Keywords: furfural, hydrogenation, perovskites

Introduction. The reduction in the availability of oil reserves and emerging environmental changes have generated interest in developing economic, efficient, and environmentally friendly technologies to transform biomass-derived molecules. Furfural is a promising platform molecule of biomass to obtain, through catalytic processes, high value-added chemicals such as furfuryl alcohol (FUR-OH), 2-methylfuran (2-MF) and tetrahydrofurfuryl alcohol (THF-OH), among others [1,2]. The catalysts of interest are perovskites due to their versatility of structural conformation[3]. In this work the synthesis, characterization, and catalytic evaluation of three pure (ABO_3) perovskites, $LaCoO_3$, $LaNiO_3$, $LaFeO_3$ and three substituted ($AB_{0.5}B'_{0.5}O_3$) perovskites, $LaFe_{0.5}Co_{0.5}O_3$, $LaFe_{0.5}Ni_{0.5}O_3$ and $LaCo_{0.5}Ni_{0.5}O_3$ previously reduced at 500°C in the hydrogenation of furfural is reported.

Experimental/methodology. The materials were characterized by X-Ray diffraction (XRD), physisorption of N_2 at 77 K, thermal programmed reduction (TPR H_2) and thermal programmed desorption of CO_2 (TPD CO_2). The hydrogenation of furfural was carried out in a batch reactor at 30 bar of H_2 pressure and 200 °C using n-dodecane and n-hexadecane as a solvent and internal standard, respectively.

Results and discussion. The characterization results show that the presence of Fe in the B cation in both pure and the substituted perovskites gives it great stability in a reducing atmosphere, avoiding the formation of metallic nanoparticles. On the other hand, in the $LaCoO_3$, $LaNiO_3$ and $LaCo_{0.5}Ni_{0.5}O_3$ perovskites, metallic Co and Ni species were detected, which also induce the formation of basic sites. Only in the $LaCoO_3$, $LaNiO_3$ and $LaCo_{0.5}Ni_{0.5}O_3$ catalysts a 100% of furfural conversion after 4 h of reaction was observed, detecting significant differences in the selectivity at 40% for furfural conversion (Figure 1). For $LaNiO_3$ and $LaCo_{0.5}Ni_{0.5}O_3$ the main product was THF-OH and FUR-OH as secondary compound, while in $LaCoO_3$ the main product was FUR-OH, followed by 2-methylfuran (2-MF) as a secondary product. These results indicate that the conversion of furfural in $LaNiO_3$ and $LaCo_{0.5}Ni_{0.5}O_3$ perovskites follows the route of hydrogenation of the C=O bond to FUR-OH and then hydrogenation of the C=C bond of the aromatic ring to form THF-OH, while in $LaCoO_3$ the hydrogenation of the C=O bond occurs to form FUR-OH, followed by the process of hydrogenolysis of the C-O bond of the hydroxyl group to form 2-MF.

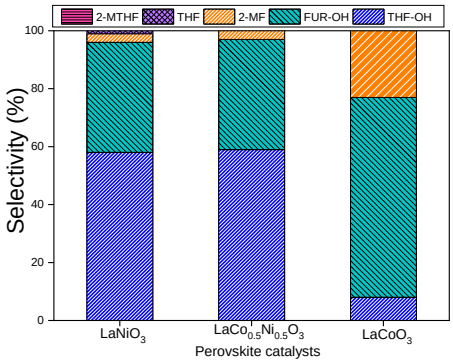

Figure 1: Selectivity at 40 % of furfural conversion.

Acknowledgments

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Carbon Supported Heteropolyacids as Recyclable Solid Acid Catalysts for the Hydrolysis of Xylan

Lea Hombach[1*], Nick Hausen[1], Alba G. Manjón[2], Markus Rose[3], Jakob Albert[4], Anna Katharina Beine[1]

[1]*Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany*
[2]*Institut Català de Nanociència i Nanotecnologia, Barcelona, Spain*
[3]*Institute of Technical and Macromolecular Chemistry TU Darmstadt, Darmstadt, Germany*
[4]*Institute of Technical and Macromolecular Chemistry Universität Hamburg, Hamburg, Germany*
[*]*lea.hombach@cec.mpg.de*

Keywords: *Biomass, Heteropolyacids, Catalyst recycling*

Introduction. In times of climate change and diminishing fossil resources, the transition to renewable raw materials such as lignocellulose is indispensable. Still, their transformation into fuels and valuable platform chemicals is challenging. Herein, the acid-catalyzed hydrolysis of xylan to the platform chemical xylose is investigated using heteropolyacids (HPAs) as catalysts.[1] They exhibit a particularly high Brønsted acidity, possess tunable redox activity and are soluble in water and most organic solvents. The latter makes them ideal for homogeneous applications but impedes their recycling and thus industrial application. To meet this challenge, the immobilization of HPAs on suitable heterogeneous supports is of high interest.[2]

Results and discussion. Initially, commercially available HPAs were tested in the hydrolysis of xylan to xylose whereby phosphotungstic acid (PTA) showed the highest activity with 90% conversion in 2 h and 81% selectivity to xylose under omtimized reaction parameters. Therefore, PTA was chosen for the impregnation on porous activated carbons (AC). Although some studies have been carried out using carbon supports for the immobilization of HPAs[3], it is not fully clarified yet whether the HPA-carbon interaction is of physical or chemical nature, which can take take place by i.e. electrostatic or acid-base-interactions of with oxygen moieties on the carbon surface. In this regard, PTA was impregnated on an oxygen-rich carbon with a high specific surface area of 1749 m^2/g. TEM analysis and EDX mapping revealed a molecular distribution of PTA on the surface. In the N_2-physisorption a significant decrease in the specific surface area to 780 m^2/g was found after impregnation. ICP confirms a high PTA-loading of 473 mg/g, which is in accordance with a significant increase of acidic sites found by NH_3-TPD. In the hydrolysis of xylan to xylose (Figure 1), PTA/AC showed a high activity with 91% conversion. The selectivity to xylose of 99% was even higher than in the homogeneous system. Furthermore, the long-term stability of the catalyst was demonstrated in batch recycling experiments, in which the catalyst could be easily seperated from the reaction system. The observed loss in activity correlates with a moderate PTA-leaching of 2–3%. Nevertheless, a moderate conversion of 44% was still achieved after 20 recycling runs. The stability of PTA/AC was further confirmed by IR and solid-state NMR-spectroscopy of the recycled catalyst. In summary, oxygen rich carbon materials were found to be promising supports to heterogenize HPAs for an efficient biomass valorization in aqueous medium.

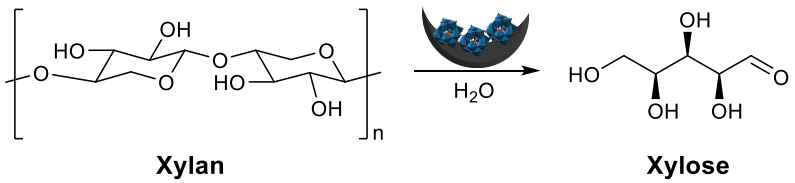

Figure 1: Hydrolysis of xylan to xylose catalyzed by PTA/AC.

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Preparation of biodiesel from spent coffee ground over hydrotalcites

M. Horňáček, M. Mališová, A. Peller

Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Radlinského 9, 812 37 Bratislava, Slovakia
michal.hornacek@stuba.sk

Keywords: SCG, coffee, biodiesel, hydrotalcites, transesterification

Critical global energy-related issues such as scarcity of fossil fuel resources, increasing price of diesel fuels, global warming and climate change crisis have necessitated the search for greener alternative fuels from renewable sources. To date, biodiesel has been regarded as one of the most viable renewable energies due to its non-toxic nature, renewability, biodegradability, favourable properties and eco-friendliness. However, about 95% of the current world biodiesel supply are produced from edible oil crops making them unfavourable and unsustainable for large scale production [1]. In this regard, there is a direct need for an alternative feedstock to avoid such controversy as well as to make large scale production economically feasible and non-competitive to food supply.

Coffee is currently the world's second largest commodity, and its consumption produces an estimated six million tons of Spent Coffee Ground (SCG) each year. For instance, approximately 650 kg of SCG are produced from one ton of green coffee beans. SCG is known to contain various organic compounds such as fatty acids, lignin, cellulose, hemicellulose, and other polysaccharides and is a suitable bio-source to produce biodiesel, activated carbon, fertilizer, sugar and even adsorbents for heavy metal ions removal [2]. Therefore, the large amount of solid waste generated from SCG which can be used for valuable product synthesis requires the development of waste management plan to ensure that it is properly utilized.

Biodiesel is commonly produced via the transesterification reaction of oil with methanol and a base catalyst which results in a fuel containing a mixture of fatty acid methyl esters (FAME) ranging from C6 to C22. However, base catalyst can only be used for transesterification of oils with FFA less than 1% to avoid saponification which can cause difficulty of ester separation [3].

Therefore, it is necessary to look for a catalytic system where the esterification of FFA and then the transesterification of triglycerides with methanol would take place. Thus, the catalyst must contain both acidic and basic centers. Hydrotalcites appear as a potentially suitable solid catalyst.

In this work, we prepared Mg/Al hydrotalcites with the addition of metals such as Ni^{2+}, Cu^{2+}, La^{3+} and Ce^{3+}. Hydrotalcites were prepared by simultanous co-precipitaion at pH = 10 and the temperature was 30 °C. Prepared hydrotalcites were characterized by available physico-chemical methods such as XRF, XRD, SEM, adsorption of nitrogen, TPD of ammonia and carbon dioxide and skeletal vibration of FTIR spectra. Mixed oxides were prepared by calcination of hydrotalcites at the temperature of 450 °C. Mixed oxides were used as a catalyst in transesterification of coffee oil with methanol. Coffee oil was obtained from spent coffee ground by Soxhlet extraction with n-hexane like a solvent. Coffee oil was treated by refining – water, acid and TOP degumming. The composition of refining coffee oil was determined by TLC, HT-GC and GC-MSD. Parameters such as conversion of acylglyrides and FAME content in the product were evaluated. Mixed oxide Ni+Mg/La+Al/HT showed the content of FAME over 99 wt. % after two step transesterification of coffee oil with methanol.

Acknowledgments

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Sustainable production of acrylic acid using renewable waste glycerol

L. Forster[1*], V. Spallina[1], C. D'Agostino[1,2]

[1] *Department of Chemical Engineering, School of Engineering, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom*
[2] *Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali (DICAM), Alma Mater Studiorum – Università di Bologna, Via Terracini, 28, 40131 Bologna, Italy.*
[*] *Corresponding Author's E-mail address: luke.forster@manchester.ac.uk*

Keywords: Heteropolyacids, Alumina, Surface Chemistry, Low-Field NMR, NMR Relaxation

Introduction. The catalysed conversion of glycerol (GLY) to acrylic acid (AA) is a highly desirable process owing to the large abundance of GLY produced as a waste by-product of biodiesel and the usefulness of AA as a platform chemical to produce high-value chemicals and commodities.
In this work, a multi-technique surface study of promising solid catalysts used for the conversion of GLY to AA is reported. In particular, γ, θ and α alumina (Al_2O_3) were modified by (i) grafting with 5 wt.% zirconia, (ii) doping with 30 wt.% silicotungstic acid (STA), and (iii) using both zirconia and STA. The aim is to rationalise the effect of these different parameters on the catalysts' structural and chemical properties and relate these properties to their catalytic activity.

Experimental/methodology. 30 wt.% STA or 5 wt.% Zr were doped onto the different alumina phases using an incipient wetness impregnation method described elsewhere. [1]
30 wt.% STA was doped onto the 5 wt.% Zr grafted aluminas using the same incipient wetness impregnation method.
Chemical and structural properties of the catalysts prepared were analysed using low-field NMR relaxation, N_2 adsorption-desorption, XRD, Laser Raman spectroscopy and differential thermogravimetry.

Results and discussion. XRD and laser Raman spectroscopy confirmed a strong interaction between STA and the γ-/θ-Al_2O_3 resulting in a distortion of the supported STA Keggin structure relative to that of bulk STA. Conversely, a much weaker interaction between the supported STA and α-Al_2O_3 was measured.

NMR relaxation demonstrated that the STA doping increases the adsorption properties of the catalyst, particularly for γ-/θ-Al_2O_3. For catalysts based on α-Al_2O_3, such effect was negligible.
Thermogravimetric/differential thermogravimetry (TGA/DTG) analysis suggested that zirconia-grafted and non-grafted θ-Al_2O_3 and γ-Al_2O_3 are suitable materials for increasing the thermal stability of STA whereas α-Al_2O_3 (both grafted and non-grafted) does not improve the thermal stability of STA.

Acknowledgments

L.F., V.S. and C.D. would like to acknowledge the EPSRC (EP/V026089/1) for supporting their research activities.

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Selective Hydrogenolysis of Glucose to Propylene Glycol over Metal-WO_x/Al_2O_3 catalysts

Aileen Hübner[1], Martin Lucas[1], Marcus Rose[1*]

[1] *Chemical Technology II, Technical University of Darmstadt, Darmstadt, Germany*
[*] *marcus.rose@tu-darmstadt.de*

Keywords: glucose hydrogenolysis, biomass, trickle bed reactor

Introduction: Due to the global population growth and the advancing industrialisation, fossil resources are the major source of carbon dioxide emissions, that can only be avoided by developing closed carbon cycles, e.g., by utilizing renewable ressources. One promising alternative is biomass, which partly consists of cellulose.[1,2] Glucose formed by the depolymerization of cellulose is a water-soluble starting material for biobased products, which is why it is well suited to study the complex network of hydrogenolysis reactions. To obtain propylene glycol and ethylene glycol, retro aldol reactions followed by hydrogenations must occur. The balance between these reaction rates is decisive for maximum yields of glycols. If the hydrogenation proceeds too fast, undesired hexitols are formed. For this reason, the interaction between the hydrogenation metal (e.g. Pd, Ni, Ru, Pt) and the retro aldol catalyzing species (e.g. WO_x) is crucial.[3] In our work, we aim at the selective synthesis of propylene glycol. Because of that, the isomerization to fructose has to occur first. For this reaction pathway, the Pd-WO_x/Al_2O_3 catalyst was shown to be suitable.[4] Hence, in our study besides palladium as hydrogenation metal, also ruthenium, platinum and copper were investigated. Furthermore, by the usage of the Pd-WO_x/Al_2O_3 catalyst, a complex kinetic study was performed in order to gain insights into the complex reaction network.

Experimental/Methodology: The bifunctional catalysts are prepared by the stepwise incipient wetness impregnation of gamma-alumina spheres with ammonium metatungstate and the metal precursor. After the calcination and reduction of the catalysts, they are tested in the glucose hydrogenolysis. The reactions are carried out in a continuously operated trickle bed reactor with an aqueous solution of glucose. For the kinetic study, reaction temperatures between 150 and 200 °C were chosen.

Results and discussion: By the usage of the Metal-WO_x/Al_2O_3 catalysts in the glucose hydrogenolysis, different product distributions were observed. With the ruthenium catalyst, the direct hydrogenation to the hexitols was favored which shows the high hydrogenation ability of ruthenium. When copper, platinum and palladium were used, hydroxyacetone (the precursor of propylene glycol) was obtained as main product. With the Pd-catalyst, the highest selevtivity for hydroxyacetone with 37 % was reached (at 190 °C and 40 bar), while 96 % of glucose was converted. In general, the hydrogenation of hydroxyacetone to the desired product propylene glycol could not be achieved. Because of that, an additional catalyst bed of the ruthenium catalyst was placed after the palladium catalyst. In this way, an almost complete conversion of hydroxyacetone was achieved. The selectivity of propylene glycol was increased from 2 % to 37 % by the usage of the combined catalysts. With respect to ethylene glycol, a selectivity of only 2 % was reached, showing the preferred reaction pathway via fructose. Besides propylene glycol, also 1,2-butanediol (S = 7 %) and glycerol (S = 2 %) were obtained. For the kinetic study, the use of various intermediates and by-products was investigated. Overall, a better understanding of the complex reaction network was achieved. By fitting the experimantal data, kinetic parameters such as activation energies were obtained.

Acknowledgments
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Hydrodeoxygenation of model fatty acid compounds of microalgae oils by Ni catalysts supported on micro/mesoporous aluminosilicates

G. Iakovou[1], A. Margellou[1], K. S. Triantafyllidis[1,2,*]

[1]*Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece*
[2]*Chemical Process & Energy Resources Institute, CERTH, Thermi, Thessaloniki, Greece*
**ktrianta@chem.auth.gr*

Keywords: Nickel bifunctional catalysts, HDO, microalgae lipids, fatty acids, green diesel

Introduction

Due to its high lipid content, algae are a renewable feedstock with high potential for the manufacture of green fuels and has gained widespread acceptance as energy source worldwide[1]. The hydrodeoxygenation (HDO) of (micro)algae shows a potential yield of liquid hydrocarbons of up to 60% depending on reaction conditions, reactor design the quality of the feedstock and the selected catalyst[2]. Ni-based catalysts were found to function better than many noble-metal catalysts[3], being also of higher abundance and lower cost. In this study, metal Ni catalysts supported on various types of micro/mesoporous materials were tested in the hydrotreatment of model fatty existing in microalgae lipids/oils to elucidate the mechanism of their conversion to the respective n-/i-paraffins via HDO, hydroisomerization and hydrocracking pathways.

Experimental/methodology

Nickel was loaded on various micro/mesoporous zeolites based on Beta, Ferrierite, ZSM-5, USY as well as ordered mesoporous aluminosilicates (MCM-41, SBA-15, etc.) with different acidic and porous characteristics, via simple incipient wetness methods followed by reduction under hydrogen. The fatty acids studied as model feeds were oleic, arachidic, linoleic and palmitoleic, being abundant in the lipid fraction of *Chlorella vulgaris* strain. The tests were performed in high pressure batch autoclave reactor and the reaction parameters (solvent, temperature, pressure, time) were optimized with regard to the different pathways, ca. decarbonylation, decarboxylation, HDO, isomerization, etc. The products were analyzed by GC-MS/FID, Karl Fischer, etc. and the catalysts were characterized by XRD, BET, XPS, TPR, etc.

Results and discussion

Analysis of the products by GC-MS showed that in the HDO of oleic acid at relatively low temperature of 250°C with 10%Ni/Beta catalyst, aliphatic n/i-alkanes in the range of hydrocarbon fuels (kerosene, diesel; C9-C18) are formed at high percentages (74-86%). In general, alkane production is favored at relatively longer reaction time (ca. 60-90 min) and with shorter chain solvents, as can be seen in Figure 1.

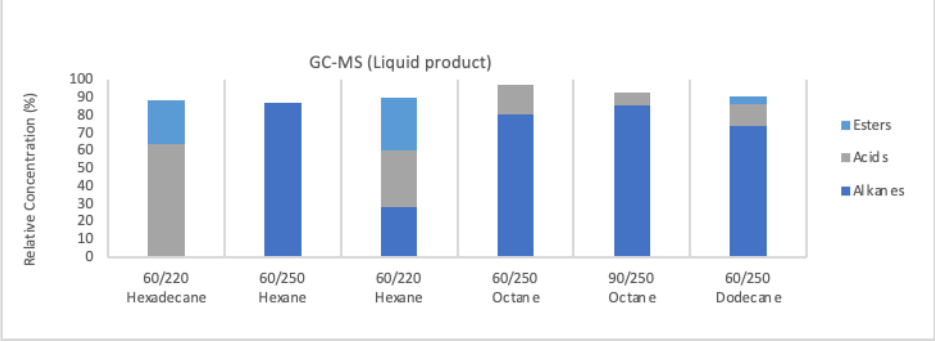

Figure 1. Relative concentrations (GC-MS) of liquid products in the hydrodeoxygenation of oleic acid over 10%Ni/Beta catalyst, at 50 bar H_2 in different solvents and varying time and temperature conditions

Acknowledgments

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Photocatalytic chemoselective cleavage of C-O bonds over palladium loaded titanium(IV) oxide

K. Imamura[1*], H. Kato[2], Y. Wada[2], K. Makabe[1], A. Onda[1], A. Tanaka[3], H. Kominami[3], K. Sato[4], K. Nagaoka[4]

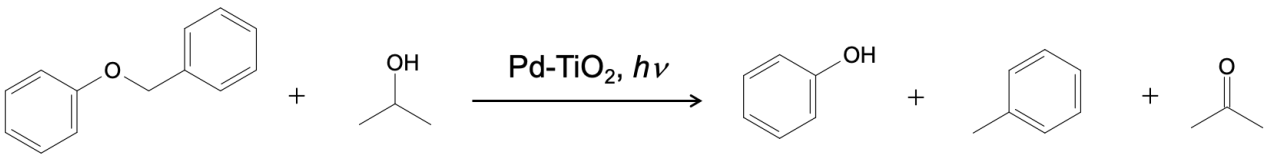
[1]*Faculty of Science and Technology, Kochi University, Kochi, 780-8520, Japan*
[2]*Faculty of engineering, Oita University, Oita, 870-1192, Japan*
[3]*Faculty of Science and Engneering, Kindai University, Osaka, 577-8502, Japan*
[4] *Graduate School of Engneering, Nagoya University, Nagoya, 464-8603, Japan*
[*]*imamura-kazuya@kochi-u.ac.jp*

Keywords: Hydrogenolysis, Photocatalyst

Introduction. Reactions that selectively cleave C-O bonds are important in organic synthesis[1]. Lignin is an amorphous polymer comprising aromatic monomers connected via oxygen bridges (C–O bonds)[2], and aromatic compounds can therefore be produced by selective cleavage of the bridges. Therefore, various catalysts have been investigated for the cleavage of lignin C-O bonds to produce aromatic compounds[3]. These reactions require severe reaction conditions (i.e., high temperatures and high H_2 pressures), which result in poor selectivity for the target materials owing to the production of by-products. Irradiation of TiO_2 with UV light results in the formation of electrons and holes, which can then participate in reduction and oxidation reactions, respectively. These redox reactions proceed at room temperature under atmospheric pressure. In this study, photocatalytic cleavage of C-O bond in benzyl phenyl ether as a model compound for lignin.

Experimental/methodology. Bare TiO_2 (50 mg) was suspended in 5 cm^3 of alcohols containing benzyl phenyl ether (50 μmol) in a Pyrex test tube, which was then sealed with a rubber septum under argon and photoirradiated at $\lambda > 300$ nm by means of a 400-W high-pressure mercury arc with magnetic stirring in a water bath maintained at 298 K. The amounts of unconsumed benzylphenylether and generated toluene and phenol were determined with a gas chromatograph.

Results and discussion. When bare TiO_2 was used as the photocatalyst, no reaction of benzyl phenyl ether occurred. We investigated Cu, Ru, Rh, Pd, Ag, Pt and Au as co-catalyst. When we used Ru-, Rh-, Pd-, or Pt-loaded TiO_2, toluene and phenol were obtained in a 1:1 molar ratio by cleavage of the C–O bond of benzyl phenyl ether without the need for H_2 gas. The Pd-TiO_2 catalyst showed much higher yields of toluene and phenol than did the other photocatalysts (scheme 1).



Scheme 1 Time courses of the amount of 1-phenylethanol remained and acetophenone formed in photocatalytic hydrogenation using glucose instead of H_2 gas.

Acknowledgments
This work was supported by a Grant-in-Aid for Young Scientists B (no. 16K18292).

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Catalytic dehydration of model xylose and real biomass pretreament hemicellulose streams towards furfural enriched products

S. P. Ioannidou[1], A. G. Margellou[1], A. Anukam[2], L. Matsakas[2], U. Rova[2], P. Christakopoulos[2] and K. S. Triantafyllidis[1,3,*]

[1]*Department of Chemistry, Aristotle University of Thessaloniki, Greece*
[2]*Biochemical Process Engineering, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, Luleå, Sweden*
[3]*Chemical Process & Energy Resources Institute, CERTH, Thermi, Thessaloniki, Greece*
**e-mail: ktrianta@chem.auth.gr*

Introduction

The valorization of hemicellulose sugar streams derived from the pretreatment and fractionation of lignocellulodic biomass comprises an important sustainability pillar in various 2nd generation biorefinery schemes. The main reactions/processes involved are the hydrolysis of oligmeric carbohydrates towards monomer sugars such as xylose, arabinose, etc. and their dehydration to the respective furans (i.e. furfural and HMF) by homogeneous or heterogeneous acid catalytic systems. The obstacles to be overcome are the tendency of furanics to rehydrate towards organic acids, i.e. formic, levulinic, etc. and/or to condensate to polymeric humins, thus decreasing their selectivity and yield. When real hemicellulose streams are involved, for example originating from the hydrothermal/mild acid or organosolv pretreatment of biomass, the co-presence of organic acids needs also to be considered.

Experimental/methodology

An optimization study was initially conducted using model xylose feed solutions in neat water, as well as in biphasic systems, e.g. water/THF, GVL, in the presence (or not) of NaCl to induce the salting-out effect and "protect" the formed furfural via in-situ extraction from the aqeuous to the organic phase. Both homogeneous (dilute H_2SO_4, H_3PO_4, HCl) and heterogeneous (ZSM-5, BETA, USY zeolites) acid catalytic systems were tested, at different reaction conditions (time, temperature and pressure). Mechanistic studies focusing on furfural stability and effect of co-presence of organic acids in the hemicellulose streams were also performed. Real hemicellulose streams, isolated from the organosolv pretreatment of beechwood sawdust, were then investigated as feed at the optimum conditions towards maximizing furfural production. Feeds and products were analyzed by HPLC, GC-MS, GC-FID, NMR, while solid catalysts were characterized by XRD, BET, ICP, acidity measurements, etc.

Results and discussion

The optimum reaction conditions towards maximum furfural yield (61% at ~100% xylose conversion) using model xylose in water were 175°C, 15 min, 10 bar N_2, with the reaction temperature being the dominating parameter in comparison to time. Sulphuric acid (H_2SO_4) was most effective compared to HCl and H_3PO_4, at low concentrations in order to minimize the subsequent conversion of furfural to acids and humins. Solid acid zeolite catalysts (ZSM-5, BETA, USY) were also very active (~100% conversion) with ZSM-5 (Si/Al=11.5) showing the highest furfural yield of 40%. Co-feeding ethanol, being present in real organosolv hemicellulose streams, led to slightly lower conversion and yield, depending on the addition level, inducing at the same time the formation of furfural diethyl-acetals. Furthermore, the reactivity of various organic acids, i.e. formic, acetic, levulinic, lactc, being also present in real hemicellulose streams was also high towards furfural formation, reaching 50-70% yield at the studied conditions. The use of biphasic systems, afforded organic solvent fractions containing essentially only furfural. The results obtained from the model xylose tests were adopted and verified with the hemicellulose aqueous streams derived from the organoslv pretreatment of beechwood sawdust, where the existing H_2SO_4 (from the organosolv pretreatment) was utilized as the acidic catalysts.

Acknowledgments

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Hydrothermal stearic acid deoxygenation over (1% wt. Pd)-supported (C, SiO_2, Al_2O_3 or Nb_2O_5) catalysts

Kallyu M. de Souza, Camilo A. B. Crisóstomo, Marina C. F. Ávila, Ricardo R. Soares*

Faculty of Chemical Engineering, Federal University of Uberlandia – Av. Joao Naves de Ávila 2121, Bloco 1K, Uberlândia/MG, Brasil, 38408-100
**rrsoares@ufu.br*

Introduction.
A one-pot catalytic hydrolysis-decarboxylation reaction is one of the potential route to produce green diesel or value-added chemicals such as α-olefins by using natural fats and vegetable oil-based feedstocks. Nickel and/or palladium catalysts are good candidates to carry out both reactions sequentially in the same conditions. However, the decarboxylation of the fatty acids, which are in the feeding or produced in the hydrolysis reaction, in an aqueous reaction media is less effective and described in the literature than the organic one. Then, the main goal of this work is to investigate the stearic acid (SA) hydrothermal deoxygenation by using palladium supported on different supports (C, Al_2O_3, SiO_2, Nb_2O_5).

Experimental.
The catalysts (1 wt.% Pd) were prepared by incipient wetness impregnation of an aqueous $[Pd(NH_3)_4](NO_3)_2$ solution, dried at 120 °C and calcined at 300 °C (except on C). They were characterized by H_2-TPD, CO-chemisorption, and other techniques. The reactions were performed in a 500 mL-stirrer batch reactor at 25 bar and 250 °C during 3h by using SA/H2O/catalyst mass ratio of 1/100/5.

Results and discussion.
Heptadecene was the main organic molecule observed in the GC-FID analysis after reaction, indicating a selective decarboxylation reaction. Figure 1 reveals that the final decarboxylation conversion was reached at less than 1.5 h with all catalyst. It also exhibits the maximum specific rates after 1.5 h and the turnover frequency (TOF) as well. The results can be explained by the metallic sites density and strength.

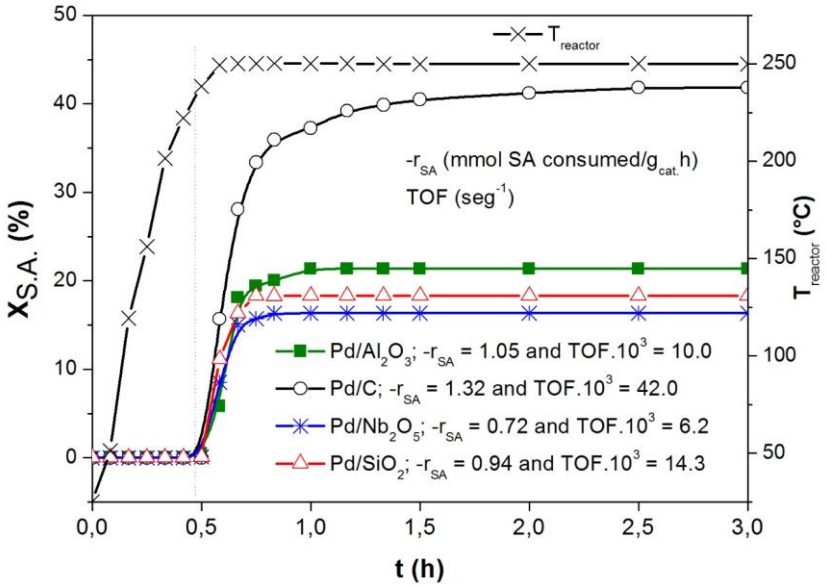

Figure 1 - SA decarboxylation/decarbonylation catalytic activities

Acknowledgments
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Selective hydrogenation of polyenes in biomass-derived cardanol over the trimetallic Ni-Co-Cu catalyst supported on morphologically controlled alumina

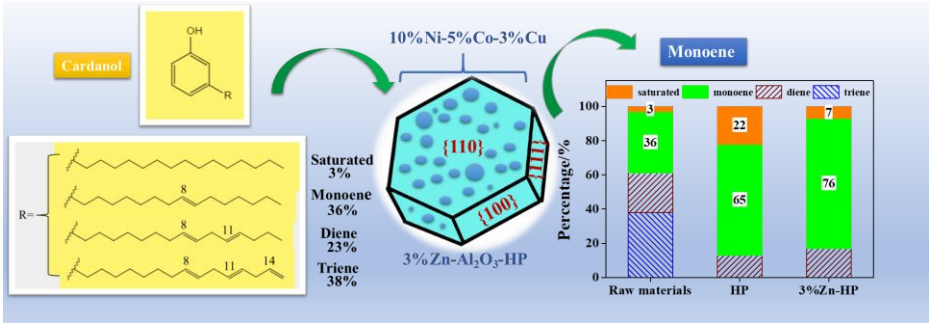
J. Ding, Z. S. Xu, H. J. Fang, X. Z. Feng, W. J. Ji*

Key Laboratory of Mesoscopic Chemistry, MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China
**jiwj@nju.edu.cn*

Introduction. The biomass-based molecules usually contain unsaturated organic groups, and catalytic hydrogenation is an effective way to achieve value-added chemicals. The effectiveness of hydrogenation process is highly defined by the selectivity toward the specific product(s). Morphology control is considered to be an effective tactic to design high performance catalyst system. [1] Cardanol can be naturally obtained from cashew nut shell liquid. The long chain hydrocarbon group of cardanol can be fully saturated, monoene, diene, or triene with different content. Renny Ni can fully hydrogenate the long chain hydrocarbon group. [2] This is unfavorable, however, to achieve high degree of cross-linking and coupling between resin and curing agent. Although the homogeneous $RuCl_3$-catalyzed transfer hydrogenation can achieve selective conversion of polyenes to monoene in cardanol, [3] the reaction is kinetically sluggish. Herein, we reported a transition metal-based Ni-Co-Cu catalyst effective for the target reaction.

Experimental/methodology. Al_2O_3 hexagonal plates (Al_2O_3-HP) and stacked hexagonal plates (Al_2O_3-SHP) were synthesized through the ion-liquid assisted hydrothermal approach. The commercially obtained spherules of Al_2O_3 (Al_2O_3-CS) was also used for comparison. The Ni-Co-Cu constituents were introduced by incepeinte wetness impregnation. The characterizations of XRD, SEM/TEM, EDS, XPS, H_2-TPR were performed for understanding the physico-chemical properties of catalysts. All the catalysts were evaluated in a small-sized high pressure continuously stirred tank reactor under a set of conditions.

Results and discussion. We reported a heterogeneous non-precious trimetallic catalyst for the first time for selective hydrogenation of polyenes in cardanol. By controlling morphology plus Zn doping of Al_2O_3 support, we accomplish highly selective hydrogenation of triene/diene into monoene with variable ratio. The larger sized Ni entities with higher electron density on Al_2O_3-HP are more favorable for activating triene/diene responsible for a high potential of selective hydrogenation. The Ni^0 fraction is comparatively lower while the mean particle size of Ni^0 is the smallest with lower electron density on commercially obtained γ-Al_2O_3 spherules (Al_2O_3-CS). The latter kind of Ni entities is more favorable for activating hydrogen to generate highly reactive H species accounting for a strong potential of full hydrogenation. Over a fine-tuned 10%Ni-5%Co-3%Cu/3%Zn-Al_2O_3-HP under the optimized conditions (7.5% cardinal in *n*-butanol, 2.5 MPa H_2, 80°C, 3.5 h), as high as 76% monoene can be obtainable. Note that the reaction over the current catalyst system becomes kinetically much faster (within 3.5 h). Ni-Co-Cu synergism and low content Zn-modification of Al_2O_3 (110) facet are recognized to be essential to achieve the aim of this study.



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Cobalt porphyrin-based catalyst for the furfural conversion to succinic acid

Anjali Kaiprathu[1*], Shun Nishimura[1*]

[1] Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

[*]Email: anjaliballa123@gmail.com, anjali@jaist.ac.jp, s_nishim@jaist.ac.jp

Keywords: Porphyrin, Cobalt-porphyrin, Biomass conversion, Furfural, succinic acid.

Introduction: Metallo-porphyrins are fascinating macro-molecules due to their applications in industrial and academic research, especially due to their significant role in biological reactions.[1,2] Transition metal-based organo-metallic complexes have a wide range of catalytic applications due to their immense redox potential.[3] However, some problems associated with the homogeneous metallo-porphyrin catalyst are oxidative degradation of porphyrin and the difficulty in separating the products and recovering catalysts. Further to achieve the improved stability and efficiency of these complexes, it can be immobilized solid supports such as carbon nanotubes due to its unique structural characteristics, high surface area, and the lack of solubility in most solvents.[4] In this work we introduced Co^{2+} in porphyrin and covalently immobilized on multi-walled carbon nano-tube (CNT), and explored its catalytic activity for the oxidation of furfural to succinic acid.[3,5] Currently succinic acid is producible by oxidation of butane and 1,4-butanediol, carbonylation of ethylene glycol, and fermentation of saccharides. Therein, synthesis of succinic acid through the oxidation of furfural is examined by as-prepared eco-friendly catalyst of cobalt porphyrin-based catalyst.

Experimental methods: The meso-tetrakis (carboxyphenyl) porphyrinatocobalt(II) (Co-TCPP) was prepared and characterized by FT-IR, UV-Vis, TGA, powder XRD, ^{1}H NMR, and mass spectroscopy. Subsequently, the CNT-supported Co-TCPP was screened for its activity at the oxidation of furfural with O_2 molecule.

Results and discussion: The amino-functionalized CNT-supported Co-TCPP (Co-TCPP/CNT-NH_2) exhibit promising catalytic properties for oxidation of furfural to succinic acid with excellent conversion of 76.0 % with 78.9% selectivity at moderate reaction conditions, as listed in **Table 1**. The product was confirmed by HPLC and GC-TOFMS studies. Further, the catalyst was reusable for several cycles and succinic acid was obtained as the major product constantly. In summary, the simple cobalt-porphyrin-supported catalyst was successfully able to proceed the selective aerobic oxidation of furfural to succinic acid with molecular oxygen without any co-catalysts, which generally required for the activation of molecular oxygen by metal complexes.

Table 1: Furfural oxidation using various Cobalt-porphyrin catalysts in the presence of molecular oxygen.

Catalyst	Conv. /%	Yield (Selectivity for succinic acid) /%			Carbon mass balance /%
		Succinic acid	Maleic acid	Fumaric acid	
Co-TCPP/CNT-NH_2	76.0	60.0 (78.9)	3.0	4.3	53.9
Co-TCPP/CNT	73.5	41.0 (55.8)	1.9	2.8	36.6
Blank	5.4	0 (0)	4.7	1.8	5.2

Reaction conditions: Furfural (1.0 mmol), Catalyst (20 mg), 100°C; 20 h, O_2 (1.0 MPa), water (3 mL).

Acknowledgements

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Microkinetic modeling guided Catalyst Design for hydrodeoxygenation of bio-oil

D. R. Kanchan[1], A. Banerjee[2*]

[1,2]*Department of Chemical Engineering, Indian Institute of Technology Ropar, Rupnagar, Punjab, India*
[*]*arghyab@iitrpr.ac.in*

Keywords: Brønsted-Evans-Polanyi (BEP), Catalysis, Density Functional Theory (DFT), Furan hydrodeoxygenation (HDO), Microkinetic Modeling (MKM).

Introduction: Rising crude oil prices and depleting fossil fuel reserves have led to the search for alternative sources of fuel and chemicals. Biomass pyrolysis derived bio-oil is a promising alternative, but the bio-oil is rich in oxygen and requires a catalytic hydro-deoxygenation step (HDO) to transform it into valuable fuels and chemicals. In this work, a combined Density Functional theory (DFT) and microkinetic modeling (MKM) based approach is employed for understanding the HDO activity of large bio-oil molecules (example furan) on mono and bimetallic transition metal (TM) surfaces. A similar approach has been previously applied to small molecules, but not for heterocyclic molecules like furan. In this work, using furan and O binding energy as descriptors in the MKM model, suitable HDO catalysts for the formation of oxygenates, ring saturated compounds and deoxygenated products are identified.

Experimental/methodology: For developing energetics of the reaction network spin-polarised DFT calculations were performed as implemented in Vienna Ab-initio Simulation Package (VASP)[1,2]. An energy cut-off of 450 eV and the revised PBE (revPBE)[3] exchange-correlation functional were implemented with vdW corrections[4,5] that account for weak long-range dispersion interaction. The energetics obtained was used in an MKM to obtain selectivity and rate plots for the different HDO products as a function of the furan and O binding energies.The MKM was developed using the descriptor-based analysis approach as in CatMAP[6] developed at Stanford university.

Results and discussion: Brønsted-Evans-Polanyi (BEP) relationships were developed for all elementary steps of furan activation to tetrahydrofuran (THF), open-chain alcohols, aldehydes and olefins on mono and bimetallic TM surfaces. Open-chain oxygenates were the dominant product on Pt, Ir, Pt, Rh and Pd while metals with strong oxygen binding energies (Ru and Co) facilitated C-O scission to form deoxygenated products. MKM analysis revealed the product selectivity to be a strong function of the reaction temperature. The range of binding energies of the descriptors which gave the maximum turnover frequency (TOF) for each product was also identified. The combined DFT and MKM analysis allows for accelerated catalyst discovery for HDO of biomass-derived bio-oil.

Acknowledgements

The authors acknowledge the use of high-performance computational facilities from the National Supercomputing Centre (NSCC) Singapore (https://www.nscc.sg) through project ID 13002533 and the National Supercomputing Mission (NSM) for providing computing resources of 'PARAM SMRITI' at NABI, Mohali.

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Effect of zeolite framework on the efficiency of implanted Ti active sites for methyl oleate epoxidation

S. Klinyod[1], T. Sooknoi[2], C. Wattanakit[1*]

[1]*Department of Chemical and Biomolecular Engineering, School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand*
[2]*Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Chalongkrung Road, Ladkrabang, Bangkok 10520, Thailand*
[*]*Corresponding Author's email; chularat.w@vistec.ac.th*

Introduction. The development of isomorphically substituted transition metals, especially the Ti atom, in a zeolite framework is one of the most promising perspectives for Lewis acid catalysis. In this contribution, we demonstrate the effect of the zeolite framework on the efficiency of incorporated Ti active sites in different zeolite topologies, such as MFI and BEA. It is observed that the zeolite framework can affect the structure of embedded Ti active species, confirmed by the UV-Vis DRS technique. The isolated tetrahedrally coordinated Ti active species has been successfully incorporated into the BEA zeolite framework (Ti-BEA). In contrast, the ZSM5 (MFI) framework primarily composes of tetrahedrally polymeric Ti species.[1] To demonstrate the effect of the zeolite framework on the catalytic performance in methyl oleate epoxidation, the isolated tetrahedral Ti active sites in the BEA framework show superior catalytic activity in terms of methyl oleate conversion and epoxide selectivity compared to polymeric tetrahedral Ti-containing in ZSM5 zeolite (Ti-ZSM5). Noticeably, the product distribution obtained from Ti-BEA and Ti-ZSM5 catalysts is completely different. These observations relate to the fact that the differentiation of the electronic property of Ti active species could be obtained when incorporating in the different zeolite framework, eventually changing the catalytic activity of the catalyst.

Experimental/methodology. The isomorphic substitution of the Ti atom in the ZSM5 and BEA zeolite framework is achieved by using the post-synthesis method. The consecutive chemical reactions of the dealumination and titanation reaction are applied for implanting the Ti atom into different zeolite frameworks. The catalytic activity of as-synthesized catalysts is evaluated in methyl oleate epoxidation.

Results and discussion. The differentiation of the zeolite framework can induce the formation of different incorporated Ti active structures. The UV-Vis DRS spectra point out that the Ti active species in the BEA framework are mainly isolated four-coordinated Ti sites, verified by the strong adsorption band of 214 nm. On the other hand, the tetrahedrally polymeric Ti active sites mostly contained in the ZSM5 framework are confirmed by the adsorption band of 248 nm,[1] as shown in Figure 1A. To illustrate the effect of zeolite framework and Ti species in a catalytic activity, the obtained catalysts are employed in the catalytic transformation of methyl oleate to their corresponding epoxide compounds. Obviously, the product selectivity derived from different Ti active species is remarkably changed. The further transformation of the epoxide product to the hydrolyzed product can be suppressed when the isolated Ti active site in BEA zeolite is applied as a catalyst. In contrast, the polymeric tetrahedral Ti sites in the ZSM5 catalyst facilitate the conversion of epoxide product to methyl 9,10-dihydroxystearate (MDI) compound through consecutive hydrolysis reaction, as illustrated in Figure 1B. These observations inspire the rational design of the Ti active species toward controlling the catalytic activity of the catalysts.

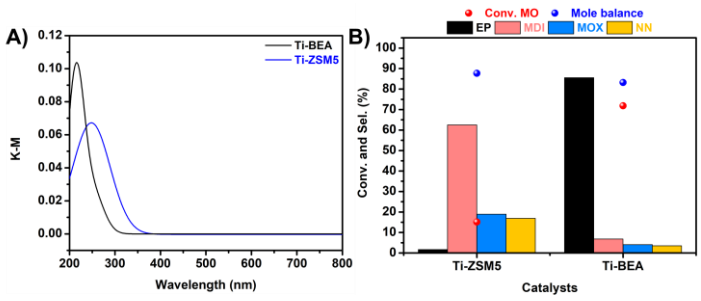

Figure 1. A) UV-Vis spectra of Ti-ZSM5 (blue) and Ti-BEA (black) and B) the catalytic performance of different catalysts.

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Production of biomass-derived polyalphaolefin-grade lubricant through aldol condensation reactions

Sang Hyeok Ko, Dinesh Kumar Mishra, Young-Woong Suh*

Department of Chemical Engineering, Hanyang University, Seoul 04763, Republic of Korea
**ywsuh@hanyang.ac.kr*

Keywords: lubricant, aldol condensation, hydrodeoxygenation

Introduction. As the world population increases, the usage and production of lubricants tend to increase every year. Most lubricants are produced from mineral oil, but due to raw material depletion and environmental problems, the technology for producing lubricating oil from unused biomass has recently been getting attention. However, the development is currently in an early stage [1,2], and it is necessary to develop a lubricant manufacturing technique with different physical properties suitable for the purpose. Thus, we developed a strategy to obtain polyalphaolefin-grade lubricants (PAOL) through a series of reactions using homogeneous and/or heterogeneous catalysts in a batch reactor.

Experimental/methodology. As depicted in Figure 1, C16 synthesis was conducted through self-condensation of octanal produced by chemical conversion of pentose and hexose derived furan derivatives. The synthesized C16 was condensed with ketones followed by aldol condensation and hydrodeoxygenation, affording PAOL product. All aldol condensation reactions were conducted in a glass reactor and autoclave batch reactor using homogeneous and heterogeneous catalysts, respectively. Hydrodeoxygenation experiments were performed in a batch reactor with heterogeneous catalyst.

Results and discussion. The optimal octanal self condensation reaction conditions were chosen to achieve a high yield of C16 ketone (Y_{C16} = 80%). The synthesized C16 ketone was condensed with C11 ketone, and then hydrodeoxygenated over Pd/$NbOPO_4$ to the target product, C27 alkane. The hydrodeoxygenation product of C27 alkane was analyzed through GC-MS (Figure 2) and ^{1}H-NMR techniques, confirming the successful synthesis. The high-purity C27 alkane was recovered by being separated from the hydrodeoxygenation product.

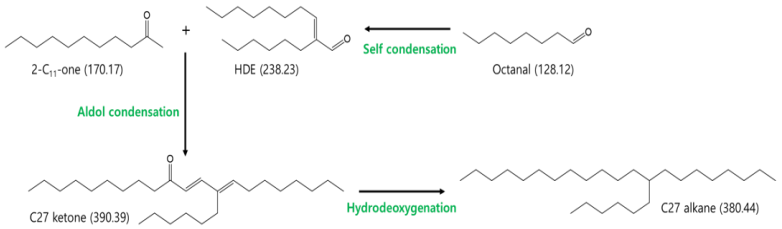

Figure 1. Reaction pathway for the synthesis of polyalphaolefin lubricant (C27)

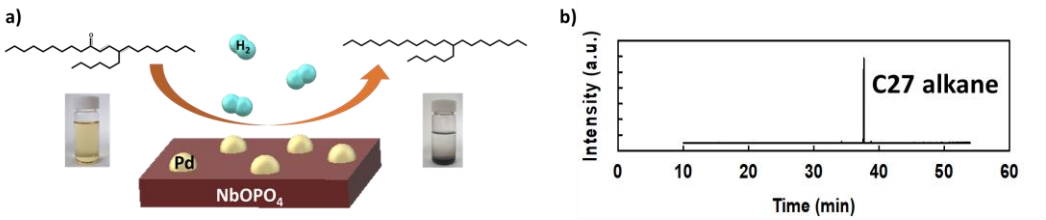

Figure 1. a) Hydrodeoxygenation of C27 ketone and b) GC-MS result of the hydrodeoxygenation product.

Acknowledgments
The work was supported by the National Research Foundation of Korea under the Ministry of Education, Republic of Korea (NRF- 2020M1A2A2080856).

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The role of the mixed oxides based catalysts in the production of higher alcohol and acetates from ethanol

J. Kocík[1*], Z. Tišler[1], J. Mück[2], K. Frolich[2], M. Hájek[2]

[1]*ORLEN UniCRE a.s., Revoluční 84/1521, Ústí nad Labem 400 01, Czech Republicirst author's Institution, City, Country*

[2]*University of Pardubice, Faculty of chemical-technology, Studentská 573, Pardubice 532 10, Czech Republic*

[*]*Corresponding Author's jaroslav.kocik@orlenunicre.cz*

Keywords: Ethanol, butanol, Guerbet reaction, mixed oxides, Tishchenko reaction

Introduction. The decreasing amount of fossil resources and climate change lead to the intensification of research in the field of the use of renewable raw materials and waste recycling. One of the promising starting materials may be an ethanol. Today,ethanol is obtained through a fermentation process from sugar containing substances . Commonly, ethanol is mainly used as a biofuel in gasoline. However, its potential can be found in the preparation of important chemicals such as ethylene, butanol, hexanol, ethyl acetate and butyl acetate. These substances are important solvents and components in the preparation of plastics. In case of higher alcohols such as butanol and hexanol which can be prepared by the multistep Guerbet reaction, consisting of: dehydrogenation, aldol condensation and hydrogenation, respectively., The Tishenko reaction can be utilized for the acetates synthesis. . Both reactions require the presence of an acid-base catalyst. Therefore, the catalyst plays a key role, as its properties strongly influence the selectivity to the desired products.

Experimental/methodology. The mixed oxides based catalysts were prepared by co-precipitation method, where the calcination temperature was foundby TGA analysis. The structure of the catalyst was studied by XRD and the chemical composition by ICP-OES. N_2-physisorption and Hg-porosimetry were used to study of the catalyst pore size distribution. A key parameter was the study of the active sites, where acid-base centers were determinated by TPD techniques and reduction properties by TPR-H_2. The catalysts were tested in stainless steel fixed bed reactor under different reaction conditions. The catalysts activity was evaluated based on the conversion of ethanol and selectvity to main products.

Results and discussion. The presence of transition metals significantly increased the conversion of ethanol. However, the transition metals influenced the selectivity to desired products. It was found, that the presence of the copper enhanced the acetates formation,while the presence of nickel and cobalt improved the selectivity to butanol and hexanol. Besides the transition metals impact, it was found that acid-base properties influenced the selectivity, as the catalysts with higher total basicity showed higher selectivity to butanol.

Acknowledgments

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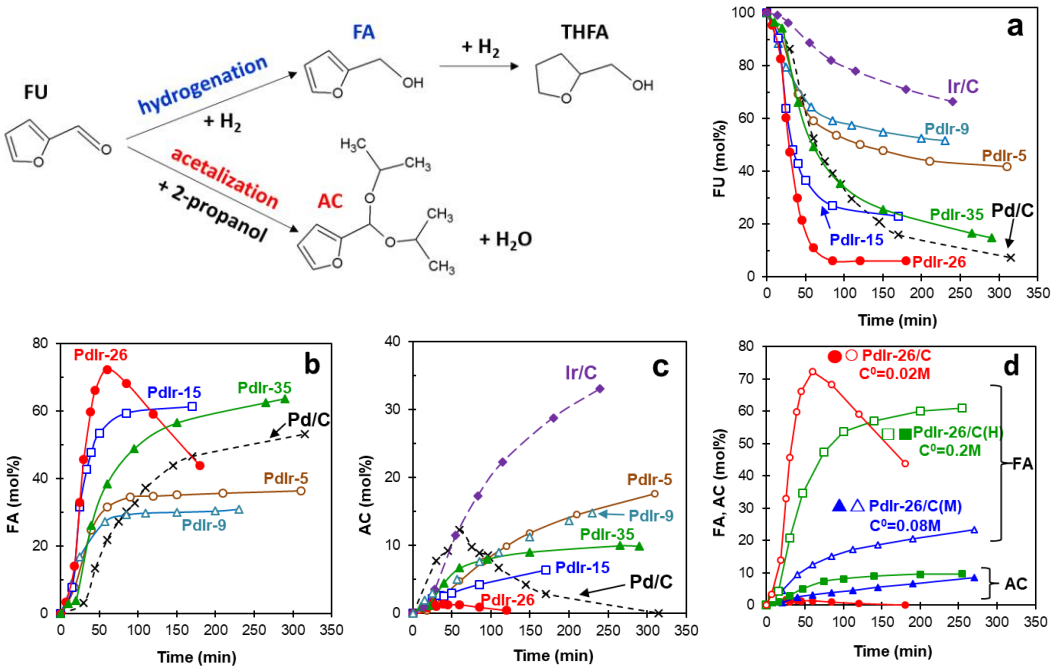
Composition-dependent activity of bimetallic $PdIr_X$/carbon catalysts in furfural conversion via competitive hydrogenation and acetalization

R. Kosydar*, E. Lalik, K. Samson, D. Duraczyńska, J. Gurgul, T. Szumełda, A. Drelinkiewicz

Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ICSC PAS
Niezapominajek 8, PL-30239 Krakow, Poland

Keywords: PdIr catalyst, hydrogenation, acetalization, furfural, furfuryl alcohol, furfural diisopropyl acetal

Introduction. Furfural (FU) platform molecule is derived from lignocellulosic biomass and can be used for sustainable synthesis of chemicals and fuels. FU hydrogenation may lead to furfuryl alcohol (FA, used for fine chemicals, lubricants, polymers, pharmaceuticals) which can be further hydrogenated to tetrahydrofurfyl alcohol (THFA, green solvent) while acetalization with alcohol solvent produces acetal (AC, potential Diesel fuel additive). The evaluation of Pd-Ir/C catalysts with various Pd:Ir surface concentration and Ir^0/IrO_x ratio for driving the reaction toward hydrogenation or acetalization is discussed.



Experimental. The catalysts were prepared by reverse water-in-oil micromulsion method. The series of nanoparticles with different Pd:Ir molar ratios were syntesized using Pd,Ir-salts solutions (c^0=0.02M) and deposited on carbon support (2%PdIr-X X=5-50mol%Ir). PdIr-26/C catalyst was also synthesized with more concentrated precursors solutions c^0 = 0.08 and 0.2M. 2%Pd/C and 2%Ir/C were also prepared. The catalysts were characterised by XRD, SEM, EDS, HRTEM/STEM, XPS, TPR, H_2 and NH_3 sorption. FU hydrogenation in 2-propanol in batch reactor under mild conditions (6 bar H_2, 35°C) was performed.

Results and discussion. The Pd/Ir bulk proportion determined surface Pd/Ir ratio, Pd-Ir alloying degree which changed the strength of hydrogen adsorption, e.g. influenced the carbonyl group hydrogenation. The highest activity (Fig. a) with the highest FA selectivity and almost no AC formation was obtained over PdIr-26/C (26%Ir) with Pd-Ir alloyed surface structure (Fig. b). On the contrary, formation of AC by FU acetalization with 2-propanol was promoted by bimetallic particles of high surface share of oxidized amorphous iridium species like IrO_x and almost without alloyed structure e.g. PdIr-5 and PdIr-9 (Fig. c). The monometallic Ir/C catalyst was also active for FU acetalization (Fig. c) but only when the active sites were generated in situ during preactivation of catalyst with H_2. There was no reactivity of Ir/C in acetalization under N_2. The change of Pd- and Ir-precursors solution concetration (c^0, Fig. d) strongly affected the Pd/Ir nanoparticles surface structure influencing the catalysts reactivity toward hydrogenation vs. acetalization.

Acknowledgments

This work is dedicated to the memory of prof. A. Drelinkiewicz. The research was founded by the statutory research found of ICSC PAS. T. Szumełda acknowledges support by Funds for Young Researchers organized by ICSC PAS.

Catalyst Screening for Stabilization of Pyrolysis Oil before Catalytic Hydrodeoxygenation into Renewable Hydrocarbon Fuels

A. P. Krebs[1], R. P. Cruz[2], A. Søgaard[1], M. Høj[1], M. Z. Stummann[3], M. Brorson[3], L. Y. Lemus-Olsen[3], A. D. Jensen[1*]

[1]*Technical University of Denmark (DTU), Department of Chemical and Biochemical Engineering, Kgs. Lyngby, Denmark*
[2]*Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal*
[3]*TOPSOE A/S, Kgs. Lyngby, Denmark*
[*] *aj@kt.dtu.dk*

Keywords: sustainable fuels, pyrolysis oil upgrading, catalytic hydrodeoxygenation, catalytic stabilization

Introduction. Fossil fuels are a major contributor to the high carbon emissions today and more sustainable alternatives are needed, especially in the transportation sector [1]. While electric cars are being implemented instead of conventional passenger cars, more sustainable alternatives remain to be found for aviation and heavy transport purposes, as these require a more energy-dense fuel source [1].

Biomass-derived hydrocarbon fuels have gained increasingly more attention as a sustainable alternative to conventional fossil fuels, as they can easily be implemented in today's engines, either by blending with fossil fuels or completely replacing them. Unfortunately, the oil produced from pyrolysis of biomass has a high content of oxygen-containing organic compounds, which leads to unwanted properties, such as poor stability and a corrosive nature [1]. Therefore, a two-step hydrotreating process is needed to remove the oxygen from the oil; the oil is first stabilized at a lower temperature to avoid reactor plugging and catalyst deactivation, before the actual HDO at elevated temperatures [2,3].

Hydrotreating catalysts can be divided into three categories: conventional sulfided catalysts, noble metal catalysts, and reduced base metal catalysts. The last two categories have been heavily investigated, but little attention has been given to the sulfur tolerance of these catalysts. As biomass-derived pyrolysis oils will contain small amounts of sulfur, it is important to take the sulfur tolerance into account, when looking for the optimal catalyst [1]. In this contribution, we will present our research into the activity and sulfur sensitivity of a range of catalysts for stabilizing pyrolysis oils.

Experimental/methodology. Catalyst screening experiments for stabilization of pyrolysis oils have been conducted on a benchscale batch autoclave setup. The catalysts were tested using the model compound furfural at high pressure and at temperatures of up to 200 °C. Addition of an organic sulfur compound to some of the experiments was used to test the sulfur sensitivity of the catalysts. The gas phase was analyzed using gas chromatography (GC) with a flame ionization detector (FID) and two thermal conductivity detectors (TCD), the liquid phase was analyzed by GC with a mass spectrometry detector (MSD) and a FID. The catalysts were characterized using XRF.

Results and discussion. An overview of the activity of a wide selection of catalysts was created from the catalyst screening experimental series. The use of the model compound furfural instead of real pyrolysis oil provided clarity on the reactions taking place during the stabilization. The experiments with sulfur addition provided insight into the sulfur tolerance of the catalysts in question. Research is ongoing to determine the catalyst best suited for stabilization purposes of pyrolysis oils.

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Promoting Effect of Ce and La on Ni-Mo/δ-Al_2O_3 Catalysts in the Hydrodeoxygenation of Vanillin

T. Kristensen[1,2*], C. Hulteberg[1,2], O. Abdelaziz[1], S. Blomberg[1]

[1]Department of Chemical Engineering, Lund University, 221 00 Lund, Sweden
[2]Hulteberg Chemistry & Engineering AB, 212 25 Malmö, Sweden
[*]*tove.kristensen@chemeng.lth.se*

Introduction.
The development of catalysts with prolonged and enhanced activity is a crucial aspect of improving and adding environmental value to the industrial hydrotreatment upgrading of lignin-based oils. It is a major challenge to develop an efficient catalyst that does not suffer from short-term deactivation due to, e.g. surface coke formation and subsequential blockage of pores and active sites [1]. The effects of rare earth metals in catalyst-support systems used in, e.g. oxidative reforming processes, have been recognized to decrease coke formation [2]. However, less attention has been given to the corresponding enhancement of the hydrodeoxygenation (HDO) process of lignin oils. The three synergistic aims of the work described in this study were: (i) to investigate the effect of adding Ce and La to the δ-Al_2O_3 support prior to thermal pretreatment in relation to textural and structural surface properties, (ii) to assess the performance in terms of activity and selectivity towards cresol in the HDO of vanillin over Ce- and La-doped NiMo/Al_2O_3 catalysts under continuous-flow conditions, (iii) and to evaluate the catalytic performance in relation to the addition of sulfur during activation of the catalyst and/or during the HDO process.

Experimental/methodology.
The catalysts were prepared using incipient wetness impregnation. Ce and La were initially added to Al_2O_3 prior to being thermally exposed to 1100 °C, whereas Ni and Mo were impregnated in separate subsequent steps and calcinated at 500 °C. HDO of vanillin was performed under continuous-flow conditions at 314 °C, 5 bar, and a WHSV 35 h^{-1} for 8 hours. The resulting liquid and gas product distribution was analyzed using GC-FID. Elemental analysis was used to evaluate carbon deposition on the used catalysts. The support and catalyst surface characteristics were evaluated using physisorption, chemisorption, XRD, TPD and TPR.

Results and discussion.
Less sintering of the doped Al_2O_3 was observed after thermally induced (1100 °C) transformation from δ- to θ-structure, suggesting a material stabilization effect by mainly La. A relative decrease in the number of tetrahedral Al_2O_3-structural sites was observed for the doped support, and blockage of such sites by mainly Ce is suggested. The addition of Ce and La resulted in a less acidic NiMo catalyst and is proposed to enhance the metal dispersion. The HDO activity tests showed sulphur dependency for both catalysts. However, enhanced selectivity of the direct HDO of vanillin was observed over the doped catalyst, and less coke was formed (Fig 1). This suggests improved characteristics and prolonged activity by doping Al_2O_3 with Ce and La.

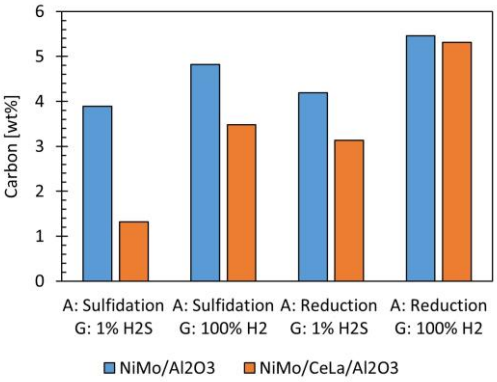

Fig 1. Carbon deposition on the used catalysts.

Acknowledgments
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Microwave-assisted synthesis of 5-ethoxymethyfurfural from carbohydrate feedstock using functionalized silica catalyst

Nidhi Kushwaha[1*], Arindam Modak[2], Ejaz Ahmad[3], Kamal K. Pant[1]

[1]*Indian Institute of Technology Delhi, Hauz Khas, New Delhi, 110016, India*
[2]*Amity University, Sector 125, Noida, Uttar Pradesh 201301, India*
[3]*Indian Institute of Technology (ISM), Dhanbad, 826004, India*
[*]*Corresponding Author: nidhi.kushwaha@chemical.iitd.ac.in*

Keywords: etherification, fructose, microwave reactor

Introduction. Catalytic upgradation of biomass-based feedstock into chemicals and biofuels is possible via several methods such as oxidation, hydrogenation, etc. The methods reported typically require high pressure environment or presence of various gases thereby increasing the cost of process and handling issues. In this regard, the etherification process has emerged as an efficient process for conversion of bio-renewable resources into 5-ethoxymethylfurfural (5-EMF) via various catalytic systems [1], [2]. Herein, we report metal-free, low cost and green heterogeneous catalytic system for developing a mechanistic study on conversion of fructose into 5-EMF. The catalyst is able to be tuned according to the demands of reaction pathway in order to increase selectivity of the reaction.

Experimental/methodology. Silica was prepared via hydrothermal method which was modified by grafting functional groups over its surface post its synthesis. The catalytic activity reactions were done in a microwave reactor via microwave heating method where quartz glass vial was charged with a known amount of fructose, ethanol and catalyst. The reactions were carried out by varying the parameters such as temperature, time, catalyst loading and substrate amount. Finally, the reaction product was filtered to separate the catalyst and quantification of products was done in HPLC, GC-FID and GCMS and kinetic studies were also done.

Results and discussion. The PXRD patterns in figure-1a show a wide peak at 22.5° indicating the formation of amorphous silica in pristine as well as in functionalized catalyst which shows that pristine structure of silica is preserved. The structure formation of silica and grafting of functional group can also be validated from FTIR spectrum in figure-1b from the Si-O-Si bond stretching of silica and bond stretching vibrations of surface functional groups. The catalytic activity studies were done at varying temperature and time in a microwave reactor which resulted in maximum 99% conversion of fructose. Furthermore, catalyst amount and substrate amount were varied which resulted in a yield of 64.39% 5-EMF at optimized conditions. Notably, time taken in microwave reactor was very less in comparison to that reported in conventional heating methods where up to 24 hours have been taken for reaction to reach maximum conversion and yield. The active acidic sites in the catalyst were mainly responsible for the reaction to occur and proceed towards equilibrium.

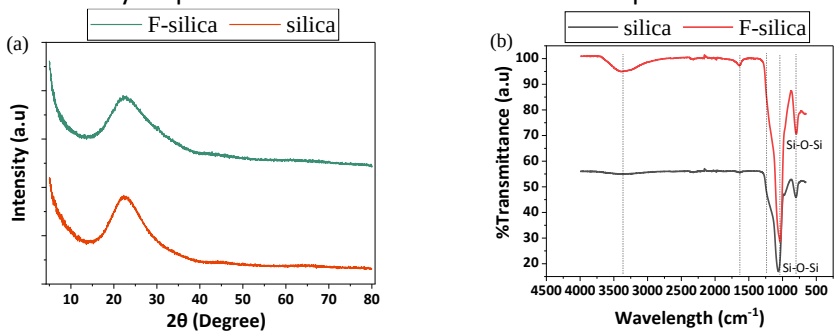

Figure 1. (a) PXRD patterns of silica and functionalized silica (b) FTIR spectrum of silica and functionalized silica

Acknowledgements

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DIRECT CONVERSION OF GLUCOSE TO HMF USING MOFS AND POLYOXOMETALATE ACIDS

M.Lara-Serrano[1*], S.Morales-delaRosa[1], J.M.Campos-Martin[1], V.K. Abdelkader-Fernández[2], L.Cunha-Silva[2] and S.S. Balula[2]

[1]Grupo de Energía y Química Sostenible (EQS), Instituto de Catálisis y Petroleoquímica, CSIC, c/Marie Curie, 2 Cantoblanco, 28049, Madrid, España.
[2]REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal.
**m.lara.serrano@csic.es*

Introduction.
The production of 5-hydroxymethylfurfural (HMF) is of great importance because it is a platform molecule of industrially significant fine chemicals[1]. In this work, glucose has been chosen as the starting material because of is the most abundant hexose contained in lignocelullulosic biomass as cellulose. The production of HMF from glucose needs two different catalysts: a Lewis-type catalyst for glucose isomerization to fructose and a Brønsted-type catalyst for fructose dehydration and obtaining HMF. For this reason, Metal Organic-Frameworks (MOF) as Lewis acid catalyst[2] and polyoxomethates (POM) as Brønsted acid catalyst have been chosen, which are respectively active for each reaction. The study of this reaction will be carried out in two ways: in the first, the MOF and POM catalysts will be added separately (MOF+POM) and in the second one, the POM encapsulates inside the MOF (POM@MOF)[3].

Experimental/methodology.
Different MOF catalysts were used in these reactions MIL-101(Cr), MIL-53(Cr), MIL-53(Al), MIL-100(Fe) and CuBTC. The inmobilization of POM in the MOF was carried out using a previously described method.[4] The reactions were performed in stirred tank reactors with a solution of 1 % glucose (0.05 g) in 5 mL of GVL-10%H_2O with the appropriate amount of catalysts.[3] The reactions were carried out at 140 °C for different reaction times (15, 30, 60, 120, 240, 360 and 480 min) and were analyzed by HPLC.

Results and discussion.
The HMF yields versus time for the two different reaction studies (MOF+POM and POM@MOF) were studied. In both cases, the formation of HMF was observed with similar yield profiles, although with some slight improvements for the POM@MOF. The best and most relevant data were those obtained with MIL-101(Cr) and MIL-53(Al) in both studies, which present an increase in performance over time up to 40 % after 480 reaction min. However, the other combinations of the different catalysts present a lower yield increase that does not exceed 20 % in any case, with stabilization from short times regardless of the method studied. Catalyst reuse studies were carried out and the most efficient was HSiW@MIL-101(Cr) with up to 6 reuse cycles. In each consecutive study cycle, a loss of POM catalyst was observed in the catalyst structure, resulting in decreased yield to HMF and increased yield to fructose in the medium.

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Bio-Isobutanol Conversion into Butene Isomers over FER, MFI, FAU and BEA Zeolites: Effect of Zeolite Structural Type on Catalyst Activity and Process Selectivity

O.V. Zikrata[1], O.V. Larina[1*], M. Vorokhta[2], I. Khalakhan[2], Yu.M. Nychiporuk[3], D.Yu. Balakin[4,5], M. Švegovec[6], J. Volavšek[6], S.O. Soloviev[1]

[1]*L.V. Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine*
[2]*Charles University, Prague, Czech Republic*
[3]*Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine*
[4]*J. Heyrovsky of Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czech Republic*
[5]*Institute of Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine*
[6] *National Institute of Chemistry, Ljubljana, Slovenia*
[*]*olga.larina@ukr.net*

Introduction. The development of processes for obtaining industrially important chemicals based on renewable raw materials is an important area of research in the sustainable chemistry. One of these processes is the dehydration of bio-isobutanol into butene isomers. The latter are the raw materials for the synthesis of various important chemicals (polybutenes, ETBE, methyl methacrylate, etc.). It is known that the production of butene isomers is possible by catalityc dehydration of isobutanol over oxide and zeolite systems [1, 2]. In particular, FER zeolites show high selectivity for linear butenes. The distribution of isobutanol dehydration products on zeolite catalysts is mostly associated with zeolite topology. We focused on elucidating the influence of the acid-base properties of FER, MFI, FAU and BEA zeolites on the conversion of isobutanol to butene isomers. Also, the deactivation behavior of the most selective catalyst was investigated.

Experimental/methodology. Commercial zeolites of FER, MFI, FAU and BEA structural types with a Si/Al ratio of 10÷68 (specified in the name of the samples) were investigated in the work as catalysts for the conversion of isobutanol. Physico-chemical characteristics of zeolite catalysts were studied by FE-SEM, XRD, N_2-ad/desorption, ^{27}Al, ^{1}H, ^{29}Si MAS NMR, ^{1}H-^{29}Si CP MAS NMR, FT-IR with pyridine, TPD-NH_3/CO_2/H_2O with MS control. The catalytic properties of zeolites were investigated in a flow-type quartz reactor unit at atmospheric pressure in the temperature range of 175-300 °C with chromatographic analysis of reagents and products.

Results and discussion. In the process of isobutanol conversion over FER, MFI, FAU and BEA zeolites the distribution of butene isomers significantly depends on structural type (see Table) of the zeolite catalyst, strength and nature of the surface acid sites. The highest selectivity toward linear butenes of 83.2 % (but-1-ene, trans-but-2-ene and cis-but-2-ene) is achieved over the FER-10 catalyst at 225 °C. Selectivity for linear butenes is more than twice as low, but also quite significant (36.8 %) is observed on MFI-40 catalyst at 175 °C after 4 h of reaction. This may be due to the presence of a larger number of strong Brønsted acid sites on FER-10 surface compared to the MFI-40 and other catalysts, which are active sites for both alcohol dehydration and alkene skeletal isomerization. The catalyst under study retains a fairly high activity after above 45 hours. The reasons for a decrease in catalyst activity were studied using ^{1}H-^{13}C CP MAS NMR and NAP-XPS methods.

Indices of isobutanol conversion over zeolite catalysts (T = 175 °C, W = 1 g/(g_{cat}·h), TOS = 2.7 h)

Catalyst	Conversion, %	$S_{linear\ butens}$, %	Selectivity, %				
			Isobutene	But-1-ene	trans-But-2-ene	cis-But-2-ene	Others
FER-10*	18.5	72.5	23.8	8.1	42.8	21.6	3.7
MFI-40	30.0	35.3	57.1	4.2	19.7	11.4	7.6
FAU-15	52.8	14.0	36.4	1.9	7.0	5.1	49.6
BEA-19	37.6	18.1	38.4	3.1	7.9	7.1	43.5
BEA-68	23.7	21.1	50.0	3.4	9.5	8.2	28.9

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Catalytic Co-pyrolysis of Beech Wood and Polyamide-6

W. de Rezende Locatel, C. Mohabeer, D. Laurenti, Y. Schuurman, N. Guilhaume*

IRCELYON, Univ. Lyon1-CNRS, UMR5256, Villeurbanne, France
** nolven.guilhaume@ircelyon.univ-lyon1.fr*

Keywords: Biomass, polyamide, catalytic upgrading, co-pyrolysis, HZSM-5

Introduction. Biomass residues and wastes can be converted into bio-liquids by pyrolysis, which can contribute to both the production of renewable fuels and the recycling of wastes. In this work, the pyrolysis of pure beech wood (BW) and of BW mixed with polyamide-6 (PA6), a nitrogen-containing plastic, little studied in pyrolysis but ubiquitous in particular in the building industry, was investigated to assess the effect of PA6 on the properties of bio-oils, obtained either by thermal pyrolysis or by pyrolysis with ex-situ catalytic treatment.

Experimental. The catalytic treatment was applied to the pyrolysis vapors that are driven across a HZSM-5 catalyst bed before their condensation into liquid products in a dedicated reactor already descibed [1].

Results and discussion. The presence of 20 wt.% PA6 in the blend affected the pyrolysis products yields and distribution (gases, liquids, chars), but also the composition of the bioliquids. In absence of a catalyst, the production of phenolic, sugar and furan compounds decreased significantly with the BW+PA6 blend compared to pure BW, and N-containing compounds derived from PA6 were found in the bioliquids (Fig. 1). When HZSM-5 catalyst was used for the treatment of vapors, the production of sugars and furans decreased and a small production of fully deoxygenated compounds was observed with pure BW. This effect was mitigated with BW+PA6 blends and the formation of deoxygenated compounds was almost totally suppressed, suggesting that the strong catalyst acid sites were poisoned. Caprolactam was by far the main product of PA6 degradation found in the bioliquids, but the N-containing by-products were different depending on the absence or presence of HZSM-5 catalyst. Mixtures of BW and PA6 in different ratios were also co-pyrolyzed in the presence of the HZSM-5 catalyst. With increasing PA6 concentrations, less gaseous products were formed, evidencing a catalyst deactivation (less cracking activity). In the liquid phase products, the production of oxygenated aromatic compounds and of fully deoxygenated compounds decreased with increasing PA6 concentrations, while the average molar mass of bio-oils and their N-content increased. It was also observed that the amount of coke deposited on the catalyst decreased as the PA6 concentration increased.

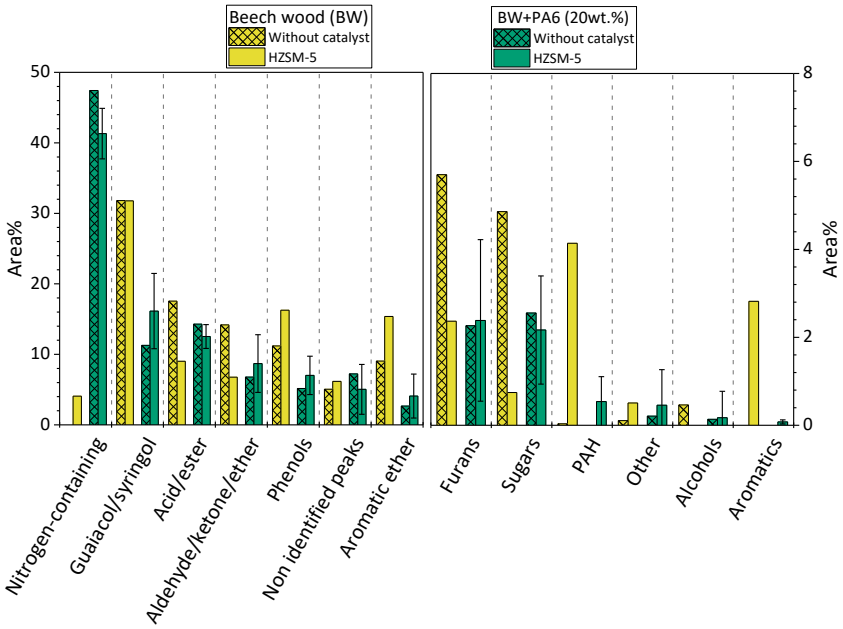

Fig. 1. Relative areas of compounds families by GC-MS for organic phases

Acknowledgments

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Catalytic depolymerization of *γ*-valerolactone organosolv processed lignin

Saravanan Kasipandi,* Sari Rautiainen, Silja Känsäkoski, Taina Ohra-aho, Juha Lehtonen

VTT Technical Research Centre of Finland Ltd, P.O. Box 1000, FI-02044 VTT, Espoo, Finland
**saravanan.kasipandi@vtt.fi*

Keywords: Depolymerization, molybdenum, organosolv lignin, phenolic monomers

Introduction. Modern biorefineries focus on valorizing cellulosic fractions of lignocellulose and major part of lignin is still used as a fuel. EU project FRACTION proposes aqueous *γ*-valerolactone (GVL) organosolv process for fractionation of different lignocellulosic feedstocks to valorise the lignin as well as hemicellulose fractions of biomass [1]. Lignin is an abundant source of aromatics and is an ideal complement or substitute to petroleum-based feedstocks [2]. In the catalytic depolymerization, lignin is depolymerized initially with solvents to form oligomers, which can be further converted into stable monomeric products via catalytic route. Herein, the lignins produced by the FRACTION fractionation process (*ie*., GVL lignin) are depolymerised via catalytic ethanolysis and ethanolysis enhanced by gaseous H_2 (hydrogenolysis) into low molecular weight products. The results of GVL lignin-derived products were compared to that of eucalyptus organosolv Fraunhofer lignin.

Methodology. Two types of catalysts namely MoC_x and MoP were synthesised and characterised using XRD, BET, XPS and SEM-EDS. The catalytic ethanolysis and hydrogenolysis were carried out in a batch reactor. Reaction parameters such as temperature, and with and without catalysts/external gaseous H_2 were studied. The depolymerised lignin oil samples were analysed using GC/MS and further information was obtained from GPC and NMR analyses.

Results and discussion. The nature of lignin properties such as interunit linkages, molecular weight, monolignol ratio and hydroxyl groups were thoroughly characterised. Non-sulfided Mo-based catalysts were prepared and studied for lignin depolymerisation reaction. As shown in **Fig.1**, MoC_x showed relatively higher monomer yields than MoP under identical reaction conditions. Moreover, use of external H_2 pressure and catalyst in the reaction system reduces char formation considerably and increase the yield of ethanol soluble oil fraction. Up to 19 wt% of monophenolics and 90 wt% of ethanol soluble fraction were achieved under supercritical ethanol reaction conditions, though increasing the reaction temperature (>280 °C) led to lower monomer yield and increase char formation. GVL lignins displayed relatively higher amounts of ethanol soluble fraction as compared to that Fraunhofer ethanol organosolv lignin.

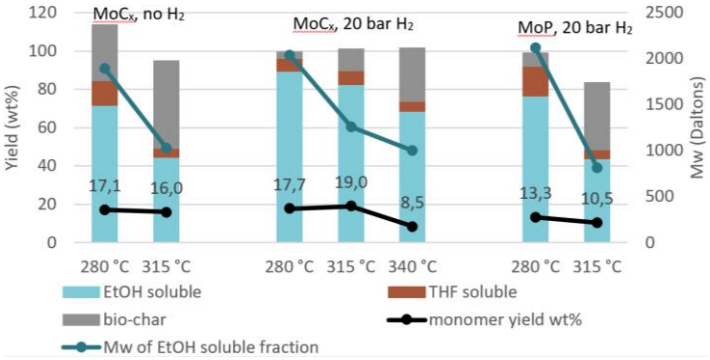

Fig.1 Comparison of catalysts and reaction conditions in depolymerisation of Fraunhofer lignin. Reaction conditions: 2 g lignin, 80 ml ethanol, 100 mg catalyst (5 wt%), 4 h

Acknowledgments

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Maximizing sustainable aviation fuel production through optimized hydroprocessing of bio-oils

Kasper Hartvig Lyng Lejre*, Jostein Gabrielsen and Magnus Zingler Stummann
Topsoe A/S, Kgs. Lyngby, Denmark
**KHLJ@topsoe.com*

Introduction

Achieving climate neutrality in the transportation sectors requires large volumes of truly sustainable bio fuels to provide long-term solutions for sectors where direct electrification is not viable. Biomass can be used as a raw material for the production of fuels with low (potentially zero) carbon footprint [1]. Biofuel processes such as hydrotreating of vegetable oils can convert biomass into fuel through well-established technologies [2]. Topsoe A/S has been developing and refining the HydroFlex™ technology since 2004 to tailor the product and optimize the yields of both renewable diesel (RD) and sustainable aviation fuel (SAF) from bio-oil feedstocks.

Experimental/methodology

In this study, the target was to produce maximum SAF yield while minimizing the loss of overall liquid fuels, SAF+RD, yield. Experiments were carried out in Topsoe's hydrotreating pilot plant facilities, using hydrotreated vegetable oil (HVO) and commercially available hydroprocessing catalyst. The tests were conducted in a once-through, fixed-bed, high-pressure pilot plant setup, loaded with 22 g of TK-920 D-wax™ which is specifically designed for dewaxing HVO and gas oil. The temperature was varied between 280 and 340°C, and the pressure applied was in the range of 40-80 barg. At each condition, gas and liquid samples were drawn and analyzed after reaching line-out. Gas and liquid analyses were carried out in order to close mass balance calculations and giving the basis for calculating yields and hydrogen consumption.

Furthermore, the feed and liquid products were subjected to a range of analytical methods to determine properties such as freezing point, simulated distillation, and density. The liquid products were fractionated to investigate the properties of the SAF and RD fractions separately. More comprehensive methods such as GC×GC-MS/FID/AED and GC-VUV were employed to give in-depth understanding of the chemical reactions taking place over the catalyst.

Results and discussion

The HVO was successfully converted to SAF and RD meeting the ASTM D7566 and ASTM D975 specifications, respectively. HVO is a liquid consisting mainly of normal paraffins with carbon numbers in the range C15-C18 resulting in poor cold flow properties. HVO produced by hydrotreating of vegetables oils or animal fats typically has a freezing point in the range of 22-28°C depending on the specific feedstock used. In order to meet SAF specifications both isomerization, to meet freezing point, and hydrocracking, to meet density and boiling point requirements, must be carried out. This is best done in hydroprocessing using a bi-functional catalyst or catalyst system tailor-made to minimize yield loss [3]. In Figure 1, transportation fuel yield, SAF and RD, is plotted as a function of SAF yield. Very high transportation fuel yields are obtained even for SAF yields larger than 20 vol% of fresh feed. The HydroFlex™ process can be applied to advanced bio fuel production where the feedstock is based on e.g. lignocelloulosic- or sewage waste. Recent pilot plant test results show that it is possible to produce SAF based on advanced bio fuel feedstock.

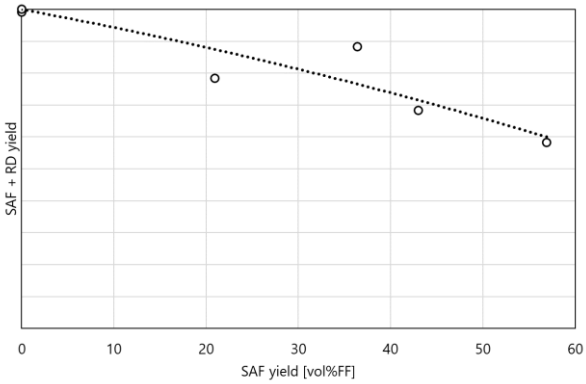

Figure 1. The overall SAF+RD yield in vol % FF as a function of the SAF yield in vol % FF.

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Reductive Amination of 5-Hydroxymethyl-2-furaldehyde catalyzed by Supported Ni-Co Bimetallic Catalysts

X. Li[1], S. Nishimura[*]

[1] *Japan Advanced Institute of Science and Technology, Nomi, Ishikawa, Japan*
[*] *E-mail: s_nishim@jaist.ac.jp*

Keywords: Reductive amination, 5-Hydroxymethyl-2-furaldehyde, Ni-based bimetal catalyst

Introduction. The manufacturing of bio-based chemicals from renewable bio-resources is an important step toward a more sustainable business. Nitrogen-containing chemicals, particularly primary amines, have long been regarded as crucial in the bulk and fine chemical industries.[1] While, in order to offer the target primary amine with a significant amount in a cost-effective and environmentally friendly method, it is crucial to design highly-efficient and selective catalysts since primary amines are more active nucleophiles than secondary and tertiary amines.[2] Herein, the reductive amination of 5-hydroxymethylfurfural (HMF), a one potential lignocellulosic biomass-derived platform chemical, to produce 5-hydroxymethyl furfurylamine (HMFA), is studied over Ni-based bimetallic catalyst by using aqueous ammonia (NH_3 aq.) and hydrogen (H_2) as nitrogen sources and reductants, respectively.

Experimental/methodology. Ni-based catalysts were prepared with a co-impregnation method, and pre-reduced in 5 vol.% H_2/N_2 flow (50 ml min^{-1}) at 500°C or 800°C for 2 h before use. A pressurized batch reactor system was conducted at the reductive amination reaction under 100°C and 0.6 MPa H_2. Reactive activity was evaluated by a GC-FID. A continuous liquid flow system was also applied for stability test.

Results and discussion. The effects of Ni:Co ratio are screened as shown in **Figure 1**. It is observed that there is an optimum ratio of Ni:Co, and then the 3wt%Ni-2wt%Co-loaded HAP (denoted as Ni3Co2HAP) catalysts is found to be the best one to afford the corresponding primary amine of 5-hydroxymethy-2-furfurylamine (HMFA) from HMF with 49% yield. It was also discovered that the decrease of reducing treatment from 800°C to 500°C (denoted as Ni3Co2HAPr500) served much higher activity (60% yield). According to TEM and XPS analysis, it indicated that not only the smaller particle size of as-gerenated CoNi but also the smaller binding energy at Ni 2*p* play a key for HMFA production with high yield, and strong interaction between Ni and Co metallic species induced these characters to be more effective. The higest HMFA yield was observed as 82% at a flow system, but stability of reactivity is still remained as next challenging subject of NiCo-catalyzed reductive amination of HMF to HMFA.

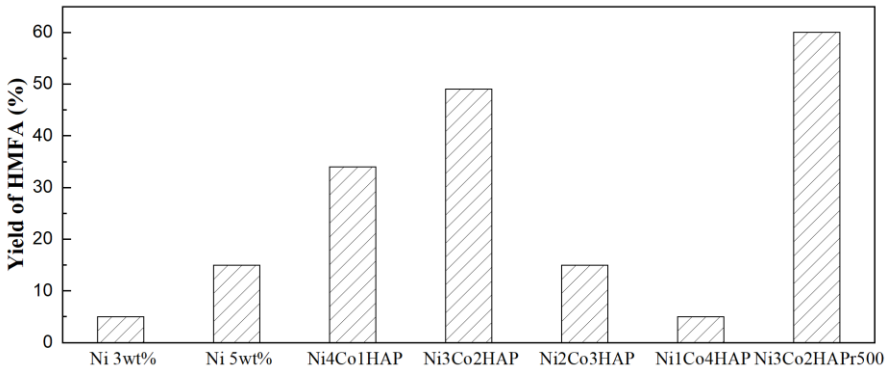

Figure 1. Yield of HMFA over HAP supported Ni-based catalysts. Reaction condition: HMF (2 mmol), 25% ammonia water (3 mL), ethanol (3 mL), catalyst (50 mg), 0.6 MPa H_2, 100 °C, 24 h.

Acknowledgments

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Enzymatic hydrolysis lignin dissolution and low-temperature solvolysis in ethylene glycol

Yushuai Sang, Yongdan Li*

Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Espoo, Finland

Keywords: Catalysis, Lignin, Ethylene glycol, Dissolution, solvolysis

Introduction. Lignocellulose, the natural composite of cellulose, hemicellulose and lignin, is the most abundant form of biomass [1]. Different from cellulose and hemicellulose, lignin is composed of aromatic units. Nowadays, cellulose and hemicellulose are fully utilized in pulping and the second-generation (2G) bioethanol industries. The 2G biofuel industry produces enzymatic hydrolysis lignin (EHL) as a low-value and large-volume byproduct [2]. As a renewable resource of aromatic molecules, EHL is an ideal feedstock for the sustainable production of commercial aromatic chemicals and fuels. Ethylene glycol is a green solvent that can be produced from the conversion of cellulose and has been widely used for the production of chemicals and fuels. In this work, EHL dissolution at room temperature and solvolysis at 200 °C in different solvents are examined, and the mechanisms of EHL dissolution and solvolysis in ethylene glycol are proposed

Experimental/methodology. EHL solvolysis was carried out in a 50 mL batch reactor. The Gaussian simulation was carried out with the Gaussian16 package using M062X simulation method in conjunction with the 6-31 g(d) basis set. The non-covalent interaction (NCI) analysis is carried out with software Multiwfn and VMD. The Forcite module in materials studio was used for molecular dynamics simulation.

Results and discussion. Ethylene glycol shows high EHL solubility and achieves complete EHL dissolution at room temperature, while methanol only dissolves part of EHL with high content of hydroxyls and β-O-4 linkages. The Gaussian simulation results indicate that ethylene glycol forms strong Van Der Waals interactions with EHL, including C-H···O and lone pair···π interactions, and these interactions break original π-π stacking in EHL, achieving complete EHL dissolution. The total monomer yields obtained from non-catalytic EHL solvolysis at 200 °C under 3 H_2 for 6 h show a positive correlation with EHL solubility, and ethylene glycol gives the highest total monomer yield, i.e., 5.5 wt%, among the solvents examined. With Ni and NaOH as co-catalysts, the total monomer yield in ethylene glycol reaches 18.8 wt% under the same reaction condition. EHL is partly depolymerized at 200 °C without a catalyst due to the strong interactions between EHL and ethylene glycol. NaOH as the homogeneous catalyst directly attracts C-O bonds in EHL and depolymerizes EHL into active monomers and intermediates. The adsorption of lignin fragments over Ni catalyst via C-O bond is hindered with ethylene glycol, and Ni catalyst mainly plays a role in supplying active hydrogen atom to stabilize the active intermediates, suppressing repolymerization side reactions.

Acknowledgments

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Co-pyrolysis of biomass and plastic to produce high-quality liquid

Zhihui Li[1*], Kishore Rajendran[2], De Chen

[1]*Norwegian University of Science and Technology (NTNU), Trondheim, Norway*
[*] *de.chen@ntnu.no*

Keywords: Co-pyrolysis, biooil, clay.

Introduction. Bio-oil is considered a potential alternative to traditional energy petroleum [1]. The most widely applied method to obtain bio-oil is pyrolyzing, however, bio-oil directly converted from biomass has drawbacks of low heating value, corrosion problems during storage and transfer and instability, because of the high oxygen content in the biomass. The oxidation content in biomass can reach 20-60 wt%, which comes from the main components of biomass, lignin and cellulose [2, 3]. Hydrodeoxygenation (HDO) process is one of the most widely used [4], whil upgrading bio-oil by HDO method has a high requirement of plant, and the catalysts for HDO are easily to be deactivated due to the coke formation. In this work, the addition of plastic into biomass in the feedstock can be considered as a hydrogen donor to achieve in-situ HDO process. At the same time, clay, a very cheap material was applied as an in-situ catalyst during pyrolysis. Aluminum pillared bentonite clay showed the potential of an alternative to commercial fluid catalytic cracking (FCC) catalyst, clay catalyzed bio-oil showed low oxygen content (6 wt%) and high liquid yield (60 %).

Experimental/methodology. Biomass was beech wood sawdust from Denmark, which contains 40wt% cellulose, 18wt% hemicellulose and 24wt% lignin. Plastic was low-density polyethylene from Sigma Adrich. Bentonite was from Sigma Aldrich and contains montmorillonite mostly. FCC catalyst was offered by Equinor, an oil company.

Experiments were carried out in a lab-scale plant, which is a semi-batch reactor in 10g scale. Gas products and liquid products were collected for further offline analysis. GC-MS and GC-FID from Agilent were applied for qualitative and quantitative analysis respectively. Additional characterization methods for catalyst, XRD, BET, SEM were applied.

Results and discussion. Aluminum pillared bentonite has a very significant improvement than raw bentonite both in surface area and acid sitee, which can benefit cracking and enhance synergic effects between biomass and plastic during pyrolysis.

Spent FCC catalyst was selected as a reference catalyst for it was found to have the very outstanding cracking ability. Aluminum pillared bentonite was found to be very competitive with FCC catalyst, both from oil quality(76.6 % and 69.9 %) and oil quantity (both lower than 10wt% of oxygen). The product oil content is mainly composed of hydrocarbon can aromatics which are also the main component of transport fuels. The comparison of biooil catalyzed by Al-pillared clay and spent FCC catalysts were shown in Table 1.

Further modification of aluminum pillared clay can be carried out to achieve even higher liquid oil yield and product distribution control.

Table 1. The comparison of liquid oil yield and components catalyzed by different catalysts.

Feed	*Catalyst*	*Liquid yield (wt%)*	*Hydrocarbons (wt%)*	*Aromatics (wt%)*	*O/C (mol)*	***O wt%***
Co-feed	/	44.7 (wax)	1.5	0.3	0.5	15.0
	Spent FCC	76.6	26.9	13.5	0.1	6.8
	Al-pillred clay	69.9	24.6	11.6	0.2	9.8

Acknowledgments
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Ru/C and Ru/TiO_2 CATALYSTS TO PRODUCE Y-VALEROLACTONE FROM LEVULINC ACID UNDER MILD CONDITIONS

Z. Ruiz-Bernal[1*], M.A. Lillo-Ródenas[1] and M.C. Román-Martínez[1*]

[1]MCMA research group, Department of Inorganic Chemistry, Faculty of Sciences and Materials Institute (IUMA). *University of Alicante, Alicante, Spain*

[*]*mcroman@ua.es*

Keywords: Ru/C catalysts; spherical carbon materials; levulinic acid; gamma-valerolactone.

Introduction.

Transformation of lignocellulosic biomass residues allows obtaining useful platform chemicals, such as levulinic acid (LA), which can be catalytically transformed into other products of interest like gamma-valerolactone (GVL) [1]. The present study is focused on the development and application of 1 wt. % Ru/C catalysts for the transformation of AL into GVL, using as catalysts supports carbon materials with different textural and chemical properties, and morphology (powder, granular and spherical). The influence of the support properties on the interaction with the metal phase has been analyzed. With the aim of designing a simpler and cheaper process, the effect of skipping the catalyst reduction treatment has been investigated.

Experimental/methodology.

The following carbon materials have been used as supports for the Ru/C catalysts: i) spherical carbons named IC-1 and IC-2, provided by Immutrix Therapeutics (USA), with a mean size of 0.1-0.2 mm and 0.5 mm, respectively, ii) an spherical carbon, named ACGE, from Gun-Ei Chemical Industry (Japan) (mean size 0.1-0.5 mm), and iii) commercial activated carbons named SA-30 (fine powder, <0.1 mm) and WV-1100 (granular, >1.0 mm) from Ingevity Corporation (USA). The spherical samples have been also used after milling in order to determine any influence of the support's morphology. Analogous catalysts have been prepared using TiO_2 supports, both commercial and prepared for this purpose.The supports and catalysts have been characterized by physical adsorption of gases (N_2 at -196 °C and CO_2 at 0 °C), programmed temperature desorption and reduction (TPD and TPR, respectively), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy coupled to EDX (TEM-EDX). The catalysts have been tested under the following reaction conditions: 0.445 mL LA, 0.130 g catalyst, 15 bar H_2, 1 h and 70 °C.

Results and discussion.

All the reduced Ru/C catalysts give very good GVL yield (60-70%). However, in the case of the unreduced catalysts, a very important effect of the carbon material properties on the catalytic activity has been found. Surprisingly, the catalysts prepared from the spherical supports are as active as the reduced counterparts. TPR and TEM-EDX results reveal that under the mild reaction conditions, the *in situ* metal reduction takes place, being the size of the resulting particles very strongly dependent on the content of surface oxygen groups on the carbon support [2]. Such surface oxygen content is lower in these spherical carbons than in the studied activated carbons. Data obtained using the milled spherical supports show that the morphology *per se* is not responsible for the good catalytic properties. Thus, efficient catalysts with high activity, reusability, and convenient handling can be prepared using appropriate carbon materials as supports.

Reduced Ru/TiO_2 (prepared with commercial TiO_2) catalysts lead to 77% GVL yield, being as competitive as Ru/C reduced ones, however the unreduced samples show a low activity similar to that of Ru/C prepared with activated carbons. This fact has encouraged the study, still in progress, of using non-reduced Ru/TiO_2 catalysts to better understand the role of the support surface chemistry in the metal support interaction and particle size.

Acknowledgments

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Syngas conversion to oxygenates over Co_2C and Co-Co_2C catalysts: CO insertion mechanism

Y. Yao*, J. Chang, Y. Zhang, N. C. Shiba, X. Liu*

Institute for Development of Energy for African Sustainability (IDEAS), University of South Africa, Roodepoort 1710, South Africa
**Corresponding Author's E-mail address: yaoy@unisa.ac.za or Liux@unisa.ac.za*

Keywords: Cobalt carbide, hydroformylation, Fischer-Tropsch synthesis, CO insertion mechanism, oxygenate

Introduction. Syngas conversion via Fischer-Tropsch synthesis (FTS) reaction system is a sustainable route for the conversion of liquid fuels and valuated chemicals and mitigation the dependency of fossil fuels [1]. Metallic cobalt (Co) is efficient for long chain hydrocarbon production, while Co_2C plays a pivotal role for the production of lower oxygenates [2]. It was reported that synergistic effect between Co and Co2C promotes the formation of higher oxygenates [3].

It generally believes that the complex FTS reaction system may not be controlled by a single reaction mechanism. Among them, CO dissociation mechanism and CO insertion mechanism are the two distinct classes of mechanisms. Our research group has experimentally improved that both the CO insertion and dissociation mechanisms may exist, by controlling the operating conditions and the cobalt species [3-5].

In addition, the structure, the dispersion and the amount of the cobalt species on the catalyst surface can be adjusted by catalyst pretreatment processes, which enhances the catalyst activity and stability and product distribution [4]. Although syngas conversion has been widely discussed, there is lack of discussion to understand the correlation of each possible reaction mechanism under different active phases of catalysts and /or reaction conditions. Therefore, it is worthwhile for the investigation of the linkage between the reaction environment and the reaction pathways.

Experimental/methodology. Typical industrial supports (SiO_2, TiO_2 and Al_2O_3) and reduced graphene oxide (RGO) were used for the preparation of the cobalt based catalysts. The catalyst preparation methods have been reported in our previous published papers [1, 2]. Large groups of experimental runs were conducted in changes the catalyst activation atmosphere (C_2H_4/H_2, CO, syngas and H_2), operating conditions (reaction temperature varied from 120 °C to 260 °C), and the compositions of the feed mixtures (H_2/CO, H_2/C_2H_4 and $H_2/CO/C_2H_4$).

Results and discussion. Comparison of the experimental results (activity and selectivity) and the characterization results (active phases and nanoparticle morphology), the reaction pathways (such as, chain growth reaction, hydroformylation reaction and oligomerization, etc.) have been discussed. A successive pretreatment method may be an effective, easy and cheaper tool to tune the product spectrum towards the aim products without the expensive upgrading of the existing catalyst system. The catalysts pretreated with C_2H_4/H_2, syngas and CO may control the formation of Co and Co_2C. Co2C promotes the formation of oxygenates via CO insertion mechanism. Co promotes the formation of long chain hydrocarbons via CO dissociation mechanism. The multiphase of Co-Co_2C demonstrated the production of higher oxygenates. This research attracts attention to the field of biomass/municipal wastes/coal/natural gas to value-added products including synthetic fuels, light olefins and oxygenates etc.

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Poster / The dehydrogenation and dehydration of isopropanol on the $SrTiO_3$ perovskite: A periodic DFT study

I. Lizana[1*], G. Bernales[1], Gina Pecchi[1], Eduardo J. Delgado[1]

[1] *Department of Physical Chemistry, Faculty of Chemical Sciences, University of Concepción, Concepción, Chile*

[*] *ignaciolizana@udec.cl*

Keywords: Dehydrogenation, dehydration, isopropanol, $SrTiO_3$, DFT, mechanism.

Introduction.

Alcohols are one of the most relevant biomass precursors, which may be used as platform molecules for sustainable production of several value-added chemicals and biofuels, as well. One of the potential routes to achieve this goal is the dehydrogenation and dehydration of alcohols over acid-base catalysts. In this study, the dehydrogenation and dehydration of isopropanol on the SrO and TiO_2 terminated surfaces, of the $SrTiO_3$ perovskite, is addressed by periodic DFT calculations in order to shed light on the involved mechanisms. This study reports the reaction pathways, including identification of the transition states and intermediates, and evaluation of the respective energy barriers, as well. Thus, this study provides significant insights about the mechanisms of dehydrogenation and dehydration of isopropanol on the $SrTiO_3$, not reported earlier in literature.

Methodology.

All calculations were carried out with Quantum Espresso v.7.0 software using the PBE functional as DFT method. A kinetic energy cutoff for wave functions was set at 50 Ry. A 3x3x1 Monkhorst−Pack scheme was considered for the supercell. Grimme-D3 corrections were used to account a good description of dispersion interactions. The systems for this study were built from the replication of the unitary cell of the cubic $SrTiO_3$ perovskite (spatial group 221 Pm-3 m, cell constant a = 3.905 Å) in a dimension of 4X3X1, involving a surface area of about 15.7x11.8 $Å^2$. SrO and TiO_2 terminated surfaces are composed by three slabs. To prevent interactions between periodic slabs, a 16 Å vacuum in the z direction and the dipole moment correction was employed. The isolate isopropanol previously optimized, was positioned at about 3 Å over the surface in different positions. Then, all atomic positions were relaxed during optimization including surfaces and adsorbate atoms. The convergence criteria for both energies and forces are $1.0x10^{-6}$ Ry and $1.0x10^{-3}$ Ry/a.u. The adsorption energies were calculated using the following equation:

$$E_{ads}=E_{(surface+adsorbate)}-E_{surface}-E_{adsorbate}$$

All energy barriers and transition states were obtained with the CI-NEB method, considering a convergence criterion of 0.05 eV/Å for the forces and using the Broyden optimization scheme.

Results and discussion.

The results show that the dehydrogenation occurs through a mechanism involving the dissociative adsorption of the alcohol on the SrO terminated surface, followed the nucleophilic attack of a hydride species on the previously adsorbed hydrogen atom to form molecular hydrogen and the corresponding carbonyl compound, with an energy barrier of 2.32 eV. The dehydration instead occurs by the molecular adsorption of the alcohol on the TiO_2 terminated surface, followed by various possible E1 elimination pathways leading to the formation of the corresponding alkene and a water molecule, with an energy barrier of 1.43 eV. The calculated energy barriers are in good agreement with experimental values[1].

Acknowledgments

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Investigation of metal molybdate catalysts for the hydrodeoxygenation of anisole

S. Löbner[1], S. Haida[1], C. Kubis[1], A. Brückner[1], A. Abdel-Mageed[1,*]

[1]*Leibniz-Institute for Catalysis, Rostock, Germany*
[*]*Ali.Abdelmageed@catalysis.de*

Introduction. Crude oil and its follow-up products are currently used as feedstock for a large portion of industrial, carbon-containing products contributing greatly to greenhouse gas emissions, carbon dioxide in particular [1]. Therefore, it is desirable to replace these oil-based resources with renewable ones. One option is the use of biomass extracts e. g. from pulp industry. Cellulose, hemicellulose, and lignin are polymers forming the cell wall of plants. In paper production cellulose is separated from the other components and the lignin is mostly treated as waste and burned. Depolymerization of lignin can be achieved with flash pyrolysis [2]. This produces a so-called bio-oil, a complex mixture containing highly oxygenated products, such as phenolics. The compounds are limited in their further use which make hydrodeoxygenation (HDO) of the bio-oil a necessary step in its valorization to useful chemicals. Compared to noble metals, Mo-based catalysts are cheaper alternative and described as efficient catalysts for HDO but without aromatic ring hydrogenation [3]. In this study metal molybdates were used for the HDO of anisole in the gas phase.

Experimental/methodology. The catalysts were prepared from stoichiometric mixing of ammonium heptamolybdate and metal nitrates in water followed by drying at 60°C and calcination at 450°C for 6 h. HDO was performed in a fixed bed reactor. The catalysts were used diluted with quartz. Anisole was introduced into the gas stream (a mixture of hydrogen and nitrogen) with a saturator. Before the reaction the catalysts were reduced in-situ for 2 h in pure hydrogen at 325°C. The reaction products were analyzed on-line with an Agilent 7890A gas chromatograph equipped with a Quadrex 007-624 column. All catalysts were characterized before and after the reaction using X-ray diffraction and other methods.

Results and discussion. In this work we studied $CuMoO_4$, $NiMoO_4$ and $CoMoO_4$. As a reference point we also investigated pure MoO_3. $NiMoO_4$ and $CoMoO_4$ catalysts reach almost full conversion at the start of the reaction and conversion decreases with time-on-stream (TOS). MoO_3 and $CoMoO_4$ start out with a low conversion which increases with TOS and decreases after reaching a maximum after 6 rsp. 8 h TOS. During the reaction the main products formed were benzene and phenol. However, $CuMoO_4$ and $NiMoO_4$ have a higher selectivity towards the deoxygenated products compared to MoO_3 and $CoMoO_4$. Interestingly, $CuMoO_4$ showed an increased selectivity towards toluene whereas $NiMoO_4$ shows an increased methane selectivity. For all catalysts selectivity towards deoxygenates decreases with higher TOS, whereas oxygenate selectivity increases. These findings will be discussed considering structural characterizations obtained from surface and bulk sensitive methods.

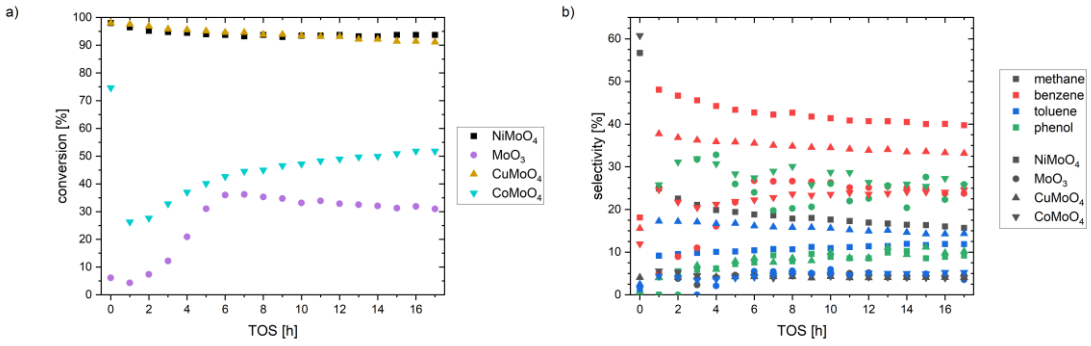

Figure 1: Changes in a) conversion and b) selectivity with time-on-stream (TOS) for metal molybdate catalysts. Conditions: 325°C; WHSV=0.31 $g_{Anisole} \cdot g_{MxMoO3+x}^{-1} \cdot h^{-1}$; GHSV=1650 $mL_{gas} \cdot mL_{cat}^{-1} \cdot h^{-1}$; atmospheric pressure

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Steam Reforming of Bio-Syngas Hydrocarbon Impurities with Ni-Co/Mg(Al)O Catalysts – Operating Parameter Effects

A. Lysne[1], I. Saxrud[1], K. Ø. Madsen[1], E. A. Blekkan[1*]

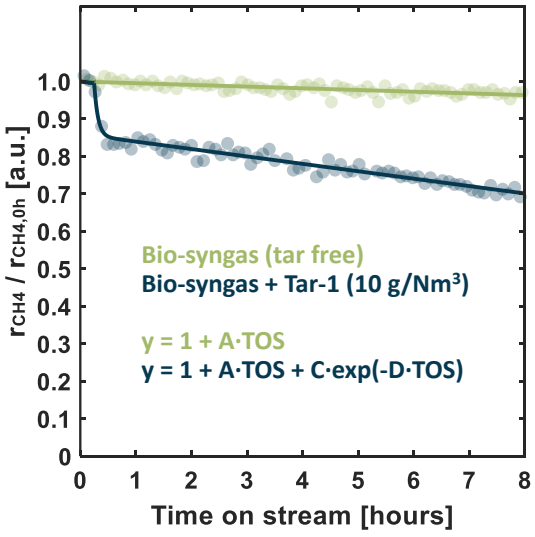
[1]*Department of Chemical Engineering, NTNU, Trondheim, Norway*
[*]*edd.a.blekkan@ntnu.no*

Keywords: Bio-syngas conditioning, tar steam reforming, Ni-Co catalysts

Introduction. Biomass gasification can provide low CO_2 emission bio-syngas for application in renewable chemical and fuel production. The gasification product typically contains hydrocarbon impurities, including condensable aromatic hydrocarbons (tars), causing downstream condensation and coking issues [1]. Such impurities can be removed by catalytic steam reforming, avoiding cost-intensive high temperature cracking and absorption strategies. Recent reviews call upon further development of bi-metallic Ni-Co systems for such applications, targeting high-stability, low-coking reforming catalysts [2].

Experimental/methodology. The Ni-Co/Mg(Al)O catalyst series was synthesized *via* calcination of hydrotalcite-like precursors, following the protocol reported by He *et al.* [3]. Fresh samples were characterized by XRD, XRF, ICP-MS, TPR, N_2-physisorption and H_2-chemisorption. Activity and deactivation experiments were performed in a model bio-syngas ($CH_4/H_2/CO/CO_2$ ratio = 10/35/25/25, molar) with and without model tar addition. The performance of a 20-20 wt% Ni-Co/Mg(Al)O catalyst was tested (8 hours on stream) at different operating temperatures (650-800 °C), steam-to-carbon ratios (S/C, 2-5, molar hydrocarbon basis), tar loading (10-30 g/Nm^3, toluene, dry syngas basis) and model tar compositions (Tar-1 = 100/0/0, Tar-2 = 75/25/0, Tar-3 = 70/25/5 wt% toluene/1-methylenaphthalene/phenol). Coke formation and sintering effects were evaluated by characterization of spent catalyst samples with TGA-TPO, Raman spectroscopy and STEM/EDS.

Results and discussion. The fresh catalyst characterization results and effects of Ni-Co ratio have been reported elsewhere [4]. Complete model tar removal at the expense of catalyst deactivation by coke formation was found at all tested conditions. The added tar carbon was well accounted for as $CH_4/CO/CO_2$ in the effluent flow. The activity and deactivation were evaluated in terms of the CH_4 reaction rate. The samples were compared considering the initial rapid activity loss and further linear deactivation function terms (see figure). The results show optimum temperature and S/C ratio conditions, minimizing overall coke formation and sintering effects. Simultaneous adjustment of the bio-syngas $H_2/CO/CO_2$ composition by WGS reaction equilibration (preparing for downstream Fischer-Tropsch applications) was demonstrated throughout the range of tested temperature and S/C ratio conditions.



Typical activity curves in tar free and model tar bio-syngas environment [4]

Acknowledgments

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Catalytic Hydrodeoxygenation of Lignin Oil for Biofuel Production

Hongfei Ma*, Wei Zhang, De Chen

Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, (Norway)
*Presenting author, hongfei.ma@ntnu.no

Introduction. Hydrodeoxygenation (HDO) has been widely used for upgrading the bio-oil [1,2]. Oxygen can be removed under H_2 pressured hydrothermal conditions in the form of H_2O. With removing of oxygen, hydrocarbons such as aromatic and aliphatic hydrocarbon compounds are produced. These hydrocarbons are the main components of liquid fuels, such as gasoline, jet fuel, and diesel. Therefore, HDO is recognized as one of the most promising routes to produce hydrocarbon fuels from lignin-derived bio-oils.

Although HDO of the lignin-derived phenolic compounds has been studied quite a lot, and among which, very active and selective catalysts were developed and reported. It is still imperative to continuously devote to the study of HDO reaction over different phenolic compounds with very high activity and deoxygenation performance. Besides, more fundamental knowledge is highly desired to have a better understanding of the reaction pathway, including the kinetic behavior of the intermediates.
Experimental/methodology. The phosphide compound MoFeP was prepared via a two-step reduction method [3]. The ruthenium (Ru) promoted catalyst was prepared by impregnating $RuCl_3$ on the above obtained MoFeP/Al_2O_3 catalyst with the corresponding amount (1 wt% Ru). Then the samples were calcinated at 500 °C for 2 h with a ramping rate of 1 °C/min. Then the obtained samples were reduced in H_2 at 400 °C for 3 h with the ramping rate of 5 °C/min. The finally obtained sample was denoted as Ru-MoFeP/Al_2O_3.
Results and discussion. Figure 1 represents the product distribution for the catalytic HDO of guaiacol over Ru-MoFeP/Al2O3 catalyst at 250 °C and 5 MPa H_2. It shows a very high activity in converting guaiacol, with cyclohexane produced as the main product, and other products are benzene, methylcyclohexane, and toluene, without any oxygen left on the products. It behaves with very good hydrodeoxygenation ability on the Ru-MoFeP/Al_2O_3 catalyst toward conversion of guaiacol. The conversion can be reached as high as 90% at the first-hour reaction. With the reaction undergoing, almost full conversion can be obtained after two hours of reaction. Still with cyclohexane and benzene as the main products. Compared with the first hour, the selectivity of cyclohexane increases a little bit, since the other hydrocarbons with unsaturated C=C bonds can be further hydrogenated. However, with the reaction going on, there are almost no changes in the selectivity of methylcyclohexane and toluene, and benzene slightly decreases a little bit. The Ru-MoFeP/Al_2O_3 catalyst shows a quite good HDO ability over guaiacol, all the oxygen can be removed, with only hydrocarbons produced.

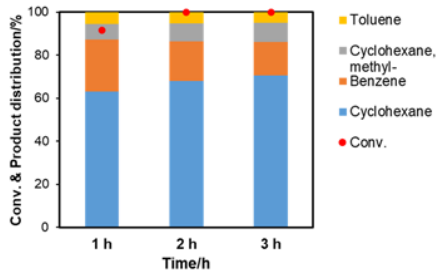

Figure 1. Results of the catalytic HDO of guaiacol. Reaction condition: 1 mL guaiacol, 50 mL Dodecane, H_2 5 MPa (at 250 °C), 0.5 g Ru-MoFeP/Al_2O_3.

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Synthesis of nickel-hierarchical zeolite nanosheet composites derived from layered double hydroxides for furfural hydrogenation

Narasiri Maineawklang, Saros Salakhum, Peerapol Pornsetmetakul, Anittha Prasertsab, Supakorn Tantisriyanurak, Chadatip Roadum, Chularat Wattanakit*

Department of Chemical and Biomolecular Engineering, School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand
**Corresponding Author's Chularat.w@vistec.ac.th*

Keywords: Hierarchical zeolite, Layered double hydroxides (LDHs), Composites, Furfural hydrogenation

Introduction. Furfural hydrogenation of biomass-derived compounds to high-value added chemicals plays an essential role in the development of sustainable resources. Nowadays, it is still challenging to design catalysts with highly dispersed metal nanoparticles (NPs) on solid support providing a high catalytic activity. Therefore, the fabrication of the hierarchical zeolite ZSM-5 nanosheets@NiAl-LDHs is presented by the growth of LDHs precursor on the hierarchical zeolite surfaces. As-synthesized material shows the high dispersion of Ni metallic nanoparticles as catalytic active sites, which can be applied in furfural hydrogenation.

Experimental/methodology. A hierarchical zeolite nanosheet (ZSM-5 NS) was prepared via a static hydrothermal method. The ZSM-5 NS@NiAl-LDHs composite was synthesized via the precipitation method at room temperature by the deposition of LDHs on the external surface of ZSM-5 NS. The composites were denoted as ZSM-5 NS@NiAl-LDHs(x) where x represents the amount of NiO (%wt). The catalytic performance of the furfural hydrogenation was investigated using a pressurized batch reactor with 0.25 MPa of H_2 at 100 ^oC for 90 min. All catalysts were reduced under 50%H_2/N_2 flow at 650 ^oC for 3 h before reaction testing. The reaction result was analyzed using gas chromatography (GC) equipped with a Porabond Q column.

Results and discussion. The XRD patterns of ZSM-5 NS@NiAl-LDHs(49) composites demonstrate the combined characteristic patterns of MFI zeolite and LDHs structures. The morphologies of the prepared ZSM5-NS@NiAl-LDHs(49) composites were investigated by STEM and EDS elemental mapping. These materials exhibit the homogeneous dispersion of nickel/nickel oxide nanoparticles on a zeolite support, confirming the uniform growth of LDHs on the ZSM-5 NS surfaces. The benefit of high metal dispersion on the zeolite surface of the ZSM-5 NS@NiAl-LDHs(49) demonstrates the high catalytic performance of furfural conversion and yield of furfuryl alcohol. For the comparison, the ones prepared by the traditional wet impregnation method and the physical mixture show only a small corresponding conversion and yield.

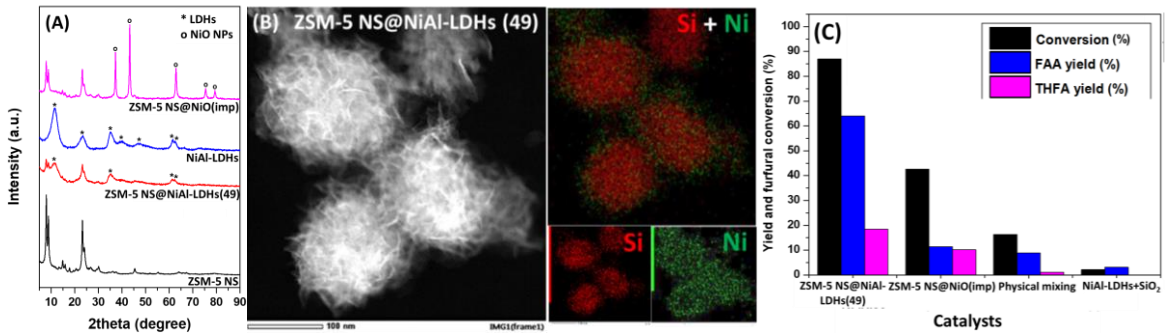

Figure 1. (A) XRD patterns, (B) STEM and EDS mapping of ZSM-5 NS@NiAl-LDHs(49), and (C) Catalytic performance in furfural hydrogenation over Ni-based catalysts with different oxide supports

Acknowledgments

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Gas phase hydroconversion of furfural catalyzed by nanostructured Pt/carbon/metal oxide xerogels

J.R. Rensch, S. Morales-Torres, L. M. Pastrana-Martínez, F.J. Maldonado-Hódar

NanoTech – Nanomaterials and Sustainable Chemicals Technologies, Department of Inorganic Chemistry, Faculty of Science, University of Granada, Avda. Fuente Nueva, s/n, ES18071 Granada, Spain
**Corresponding Author's E-mail address (fjmaldon@ugr.es)*

Introduction. Furfural (FUR) obtained from biomasss is considered as one of the most important platform molecule for the synthesis of high added-value derivatives such as furfuryl alcohol (FOL), tetrahydrofurfuryl alcohol (THFOL), 2-methylfuran, tetrahydrofuran, furan (FU), pentane, etc, which are widely used in the production of plastics, medicines, fertilizers and fuels [1]. The objective of this work is the development of sustainable FUR hydroconversion processes. Active, selective and stable catalysts working in continuous phase and mild conditions were prepared, avoiding toxicity of clasical chromite catalysts, the deactivation by coke deposition and the drastic experimental conditions (P_{H2}, T) typically used in liquid phase.

Experimental/methodology. A pure resorcinol (R)-formaldehyde (F), RF organic gels structured in microspheres were obtained in stirred reactors by inverse emulsion and always used as primary support. These microspheres were thereafter coated with SiO_2, Al_2O_3, TiO_2 and CeO_2 using the corresponding alkoxides, as precursors. The synthesis procedure was optimized for the complete gelation and curing, the solid recovered by filtering and exchanged with acetone before drying in an oven at 100 °C and finally, carbonized at 850 °C in innert atmosphere. Pt-catalysts (1% wt) were obtained by incipient impregnation of the carbon-MOx composites, dried and activated under He at 400 °C for 2h before characterization (gas adsorption, XRD, XPS and HRTEM/EDX) or reaction. The hydroconversion reactions of FUR were carried out in the gas phase using continuous fixed bed reactors under mild reaction conditions (atmospheric pressure and temperature below 200 °C). The concentrations of reactant and products were determined by GC.

Results and discussion. The heat treament provokes simultaneously the carbonization of the organic phase and the formation of the corresponding metal oxides. TiO_2 is present as anatase (JCPDS 21-1272), Al_2O_3 as δ-Al_2O_3 (JCPDS 13-0373) and CeO_2 shows the cubic fluorite structure (JCPDS 4-593). Only silica remains amorphous, together the carbon support. The coating of the carbon spheres with the metal oxide layer leads to a decrease of the overall microporosity of the supports, and consequently, the BET surface area values. The mesoporosity however is preserved or even, enhanced in the case of carbon-Al_2O_3 composite.

The formation of Pt-nanocrystals by XRD was detected only when supported on the pure carbon xerogel and carbon-SiO_2 composites. However, a very good dispersion of Pt-nanoparticles was detected in all cases by HRTEM (Figure 1). Hydrogenation and decarbonylation processes were observed, the catalytic performance being strongly influenced by the support characteristics.

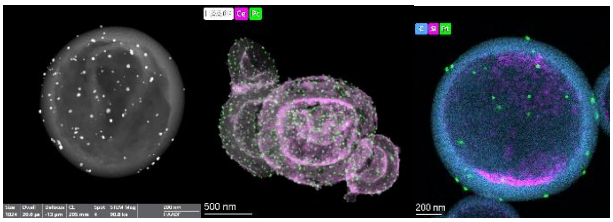

Figure 1. HRTEM images of Pt-particles on the "XC" carbon xerogel (la), XC/CeO_2-composite (b) and XC/SiO_2-composite (c).

In all cases, the MOx coatings increased the activity of the Pt-nanoparticles. At 160 °C the conversion values increased in the order XC-Pt < XC/SiO_2-Pt < XC/TiO_2-Pt < XC/Al_2O_3-Pt < XC/CeO_2-Pt. FUR is transformed into FU by decarbonylation, while FOL and THFOL were obtained by hydrogenation. At low temperature (120-130 °C) FUR hydrogenation is the main process (80% selectivity) but with increasing reaction temperature decarbonylation is favoured, reaching at around 200 °C selectivities around 70%. The most active catalysts also favour hydrogenation versus decarbonylation. No deactivation detected after several hours on stream.

Acknowledgments

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Aqueous Reduction of Biomass-derived Oxygenated Compounds by Magnetically Induced Catalysis

C. Cerezo-Navarrete[1], I. Mustieles Marin[2], A. Corma[1], B. Chaudret[2], Luis M. Martínez-Prieto[1,3*]

[1]*ITQ, Instituto de Tecnología Química, Universitat Politècnica de València (UPV), 46022 Valencia, Spain*
[2]*LPCNO, Laboratoire de Physique et Chimie des Nano-Objets, INSA, CNRS, UPS, F-31077 Toulouse, France*
[3]*IIQ, Instituto de Investigaciones Químicas (CSIC-US), Dpto. de Química Inorgánica, 41092 Seville, Spain*

Introduction. Magnetic induction heating is an emerging subject in the field of catalysis that represents a promising alternative to conventional heating.[1] It is based on the use of hysteresis losses produced in ferromagnetic materials by the presence of an alternating magnetic field. Indeed, the possibility to perform catalytic processes in solution by transforming electromagnetic energy into heat is of great advantage, since it is possible to carry out reactions which normally requires high temperatures and pressures under milder conditions.[2] In this context, the aqueous transformation of biomass-derived oxygenated compounds via magnetically induced catalysis is an attractive way to obtain fine-chemicals and fuels.[3]

Experimental/methodology. Non-coated and carbon-coated core-shell **FeCo@Ni** magnetic nanoparticles were used as heating agent and catalyst simultaneously (**Figure 1a**). The FeCo core (heating source) produces heat in close proximity to the Ni shell (catalytically active metal). In addition, the encapsulation of **FeCo@Ni** in carbon (**FeCo@Ni@C**) strongly improved the stability of this magnetic catalyst in solution, making possible its reuse.

Results and discussion. In this work, we observed for the first time a magnetic-field-controlled selectivity of hydrogenation and HDO in the reduction of biomass-derived molecules. At low field amplitudes the main product was the hydrogenation product, while at higher field the major product was the HDO product (**Figure 1b**). However, **FeCo@Ni** showed a low activity in water, mostly due to their poor stability in aqueous medium. The encapsulation in carbon circumvented this limitation and led to a stable catalyst suitable for magnetically-induced catalysis in water. In fact, **FeCo@Ni@C** efficiently hydrogenated a series of biomass-derived oxygenated compounds in aqueous medium, showing an excellent stability.

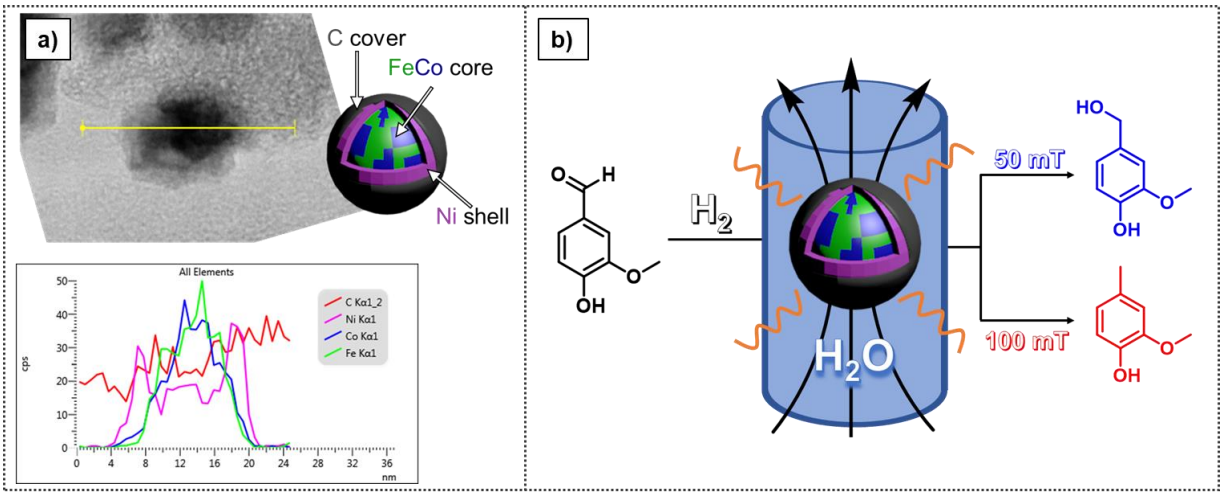

Figure 1. (a) STEM-BF image and EDX line scan profile of **FeCo@Ni@C**. (b) Magnetic-field-controlled selectivity of hydrogenation and HDO in the reduction of vanillin.

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1,5-Pentanediol production from biomass derived dihydropyran

I. Martínez-Salazar[1*], D. M. Alonso[1], M. López Granados[1], R. Mariscal[1]

[1]*Group of Sustainable Energy and Chemistry (EQS), Institute of Catalysis and Petrochemistry (IPC-CSIC), C/Marie Curie 2, Cantoblanco, 28049 Madrid, Spain.*
[*]*i.salazar@csic.es*

Keywords: biomass, 1,5-pentanediol, heterogeneous catalysis, dihydropyran

Introduction. α,ω- diols are commodity chemicals with several applications in producing acrylates, polyurethanes, plasticizers, etc. Nowadays, they are manufactured by petroleum based routes which involve several separations and high costs[1]. Obtaining these α,ω- diols from biomass constitutes an alternative attractive greener route[2]. Among the paths to produce 1,5-pentanediol (1,5-PDO) from furfural (FUR), one of the most relevant is the multistep route:1) hydrogenation of furfural to tetrahydrofurfuryl alcohol (THFA); 2) dehydration of THFA to dihydropyran (DHP); 3) hydration of DHP to 2-hydroxy-tetrahydropyran (2-HY-THP); and 4) hydrogenation of 2-HY-THP to 1,5-PDO[3].
In this study, the last two steps are integrated into one-pot reaction. However, this combination entails side reactions, such as the hydrogenation of the double bond in DHP to give tetrahydropyran (THP). To overcome this drawback, the evolution of the THP and 1,5-PDO yields with bimetallic catalysts have been assessed.
Experimental/methodology. A series of bimetallic catalysts of $RuSn_x/C$ have been synthesized by incipient wetness impregnation of Ru/C. The dried and reduced catalysts have been tested in a batch reactor at 125ºC.
Results and discussion. Differences have been spotted when comparing the catalytic activity of the reduced and dried catalysts in the synthesis of 1,5-PDO from DHP. All the catalyst achieved 100% conversion of DHP. Yet, the reduced catalysts gave higher yields towards the side product THP. Furthermore, as the Sn content in the catalyst increased, the hydrogenation ability decreased. On the other hand, the Ru/C dried catalyst gave higher yields towards the side product, THP, just as the reduced catalysts. However, when the amount of Sn increased, the yield towards 1,5-PDO followed the same trend, achieving an 81% yield of 1,5-PDO and only an 11% yield of THP with RuSn/C (figure 1). The catalysts have been characterized by XRD, TPR, XPS and N_2 adsorption isothermal to explain their catalytic activity.

Both the N_2 adsorption isotherms and the XRD do not suggest significant differences in the catalysts of the series. The XRD does not show any crystalline phase indicating that the metals are highly dispersed in the support. However, in the TPR experiments, the maximum reduction peak shifts towards higher temperatures with the Sn content. This shows that there is an interaction between the two metals, which can also be verified by XPS, since there is a shift in the binding energy. In conclussion, Sn decreases the Ru reduction ability throughout the whole $RuSn_x/C$ catalysts series. This affects mainly to the production of THP, whereas the 1,5-PDO yields keep increasing at lower Sn content. When the amount of Sn is suffitienly high, the lower reduction ability of Ru is shown in both reactions, giving lower yields of THP and 1,5-PDO.

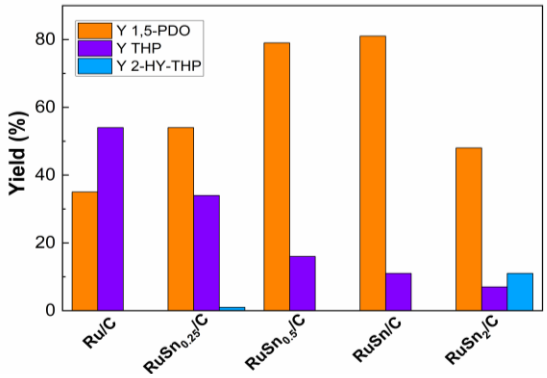

Figure 1: DHP conversion into 1,5-PDO on $RuSn_x/C$

Acknowledgments
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Hydrodeoxygenation of Isoeugenol to Produce Renewable Jet Fuel Using Bifunctional Catalysts

M. Martínez-Klimov[1*], P. Mäki-Arvela[1], Z. Vajglová[1], C. Schmidt[1], O. Yevdokimova[1], N. Kumar[1], K. Eränen[1], Dmitry Yu. Murzin[1]

[1]*Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Henriksgatan 2, Turku, 20500, Finland*
[*]*mark.klimov@abo.fi*

Keywords: hydrodeoxygenation, bifunctional, renewable, jet-fuel, binder

Introduction. The transition towards greener energy sources due to harmful emissions and respective regulations has promoted development of sustainable fuels obtained from renewable souces [1]. An attractive renewable source for fuels as well as basic, fine chemicals and various materials is lignocellulosic biomass. While lignin is considered as a waste product in certain industries, its depolymerization products can be converted through hydrodeoxygenation into hydrocarbons suitable for use as jet-fuel in existing infrastructure and technologies [2]. This is of great importance as the alternative for hydrocarbon-based jet fuel is to apply batteries, which currently is not viewed as feasible because of their excessive weight. Jet fuel consists of C_8-C_{16} hydrocarbons. In this work hydrodeoxygenation of isoeugenol, a model compound for lignin depolymerization products, was carried out in a batch reactor using bifunctional catalysts containing platinum, zeolite beta, and a binder, reflecting components of industrial catalysts, to understand their effect on the reaction.

Experimental/methodology.

A series of catalysts comprising platinum, zeolite beta and an inorganic binder were tested in the hydrodeoxygenation of isoeugenol, the main product propylcyclohexane, which is within the hydrocarbon range utilized in jet fuel. Platinum was deposited using the evaporation-impregnation method, however, the metal location was varied to change the metal-acid site proximity. Beta zeolites with two different Si:Al ratios, namely Beta-25 and Beta-300, were employed to determine the effect of acid strength. As a binder Bindzil, a type of colloidal silica, was applied. Thus, three types of catalysts for both zeolites were prepared denoted as PtB25Z*X* or PtB300Z*X*, depending on the zeolite, while *X* corresponds to the platinum location: **A** – platinum on both zeolite and Bindzil, **B** – platinum only on zeolite, **C** – platinum only on Bindzil.

Catalysts were characterized by SEM, TEM, pyridine FTIR, N_2 physisorption and ICP-AES.

Hydrodeoxygenation (HDO) reactions were carried out at 200 ºC and 30 bar of H_2 in a stainless-steel batch reactor using dodecane as solvent. The samples were taken periodically and analyzed by gas chromatography coupled with mass spectrometry.

Results and discussion.

A comparison of the catalytic results for both series of catalysts is presented in Table 1.

Table 1. Catalytic activity of PtB300ZX and PtB25ZX catalysts in hydrodeoxygenation of isoeugenol, performed in a batch reactor at 200 ºC and 30 bar of H_2.

Catalyst	Dihydroeugenol conversion (%)	TOF (s^{-1})	Liquid-phase mass balance (%)	Propylcyclohexane yield (%)	Propylcyclohexane selectivity (%)
PtB25Z**A**	78	0.08	68	56	76
PtB25Z**B**	82	0.13	62	53	75
PtB25Z**C**	53	0.09	66	21	66
PtB300Z**A**	61	0.12	78	45	77
PtB300Z**B**	46	0.06	85	37	90
PtB300Z**C**	25	0.06	83	6	88

Catalysts where Pt was located closer to the acid sites (types A and B) displayed higher dihydroeugenol conversion and propylcyclohexane yield, while deposition of platinum on the binder (type C) gave the lowest activity. Additionally, catalysts containing Beta-25 displayed higher activity than the catalysts containing H-Beta-300.

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Production of advanced biodiesel from animal wastes using supercritical conditions

J. Martínez-Triguero*, J.D. Vidal, S. Valencia, A. Chica

Instituto de Tecnología Química, Universitat Politècnica de València-
Consejo Superior de Investigaciones Científicas
Avenida de los Naranjos s/n, 46022 València (Spain)
**jomarti@itq.upv.es*

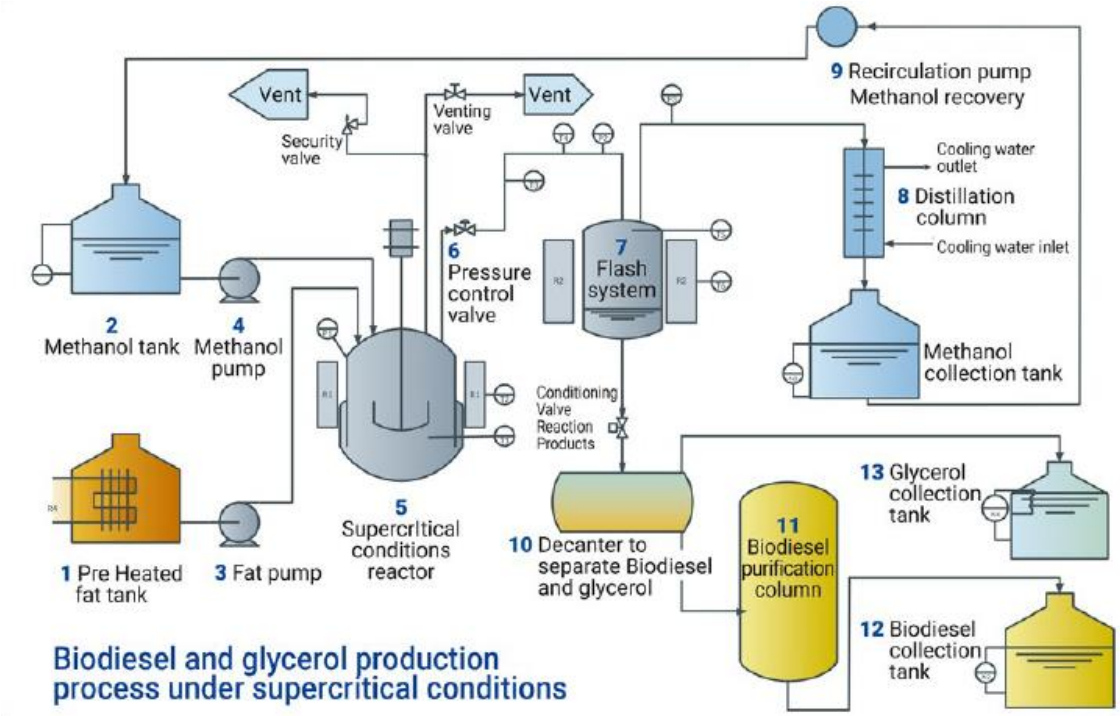
Keywords: Biodiesel, ABPs, biofuel, Superbiodiesel.

Introduction.

The valorization of animal by-products (ABPs) as is the case of animal fats from tanning industry has become of interest since the regulations limit its use in the food chain. The main objective is to demonstrate at pilot plant scale the production of biofuels from animal fat residues. These biofuels will be achieved by transesterification with methanol using supercritical conditions with the use of catalyst, incorporating glycerol derivatives as biodiesel component thus producing technical, environmental, and economic advantages on regard the traditional process.

Experimental/methodology.

Animal fats will be separated from proteins and processed continuously with methanol in a CSTR reactor at supercritical conditions (400ºC, 200ºC) using pelletized catalyst. After reaction methanol is separated from the biodiesel as shown in the figure. The throughput of the pilot plant is around 20 kg biodiesel/day.



Results and discussion.

The supercritical method takes advantage of the homogeneous phase, which improves phase solubility, increasing the reaction rate of the triglycerides and esterification of free fatty acids (FFA). Consequently, this method can process practically any kind of raw materials, such animal fats and waste vegetable oil, which are difficult to process through conventional transesterification reaction. Glycerol is incorporated into the homogeneous liquid product increasing the final yield and decreasing 80% of the carbon footprint of conventional diesel and 35% of that of first-generation biodiesel.

Acknowledgments

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Organometallic approached NiCo Nanoparticles for the Magnetically Induced Valorization of Lignin-based materials

J. Mazarío[1], I. Mustieles-Marín[1], C.W. Lopes[2], G. Mencia[1], G. Agostini[3], P.F. Fazzini[1], N. Ratel-Ramond[1], B. Chaudret[1*]

[1]*Université de Toulouse, UMR 5215 INSA, CNRS, UPS, Laboratoire de Physique et Chimie des Nano-Objets, 135 avenue de Rangueil F-31077 Toulouse cedex 4, France*

[2]*Institute of Chemistry, Universidade Federal do Rio Grande do Sul – UFGRS, Av. Bento Gonçalves, 9500, 91501-970 Porto Alegre, RS, Brazil*

[3]*CELLS-ALBA Synchrotron Radiation Facility, 08290 Cerdanyola del Vallés, Barcelona, Spain*

[*]chaudret@insa-toulouse.com

Keywords: *nickel-cobalt*, *magnetic nanoparticles*, *magnetic catalysis*, *lignin valorisation*

Introduction. Global climate change and fossil feedstock shortage have drawn considerable attention to lignocellulosic biomass. Particularly, lignin can be depolymerized into the so-called bio-oils; smaller aromatics needing oxygen removal to be profitable.[1] Thus, a catalytic system for one-pot lignin hydrogenolysis and hydrodeoxygenation is an imperative challenge. Excitingly, our latest works on magnetic catalysis on metal nanoparticles (NPs), where a catalyst combines heating and catalytic functions, accomplished reactions at reduced bulk temperatures and H_2 pressures.[2,3] Then, NiCo-NPs with various Ni:Co ratios were prepared, achieving the right balance between heating and catalytic properties, and tested in the magnetically induced hydroprocessing of lignin bio-oil and lignin models in mild conditions.

Experimental/methodology. The Ni_xCo_y NPs were prepared decomposing Ni[*i*PrNC(CH_3)NiPr]$_2$ and Co[N($SiMe_3$)$_2$](THF) complexes in the presence of palmitic acid in mesitylene at 3 H_2 bar and 120 °C. Physicochemical properties were studied by ICP, TGA, XRD, WAXS, HR-TEM and XAFS, while magnetic by VSM and SAR. Catalytic tests were carried out in liquid phase with 1.0 mmol substrate, 0.7 mmol dodecane (IS), 3 H_2 bar, and 5 mL solvent in a 100 mL glass batch reactor at the center of a 300 kHz coil.

Results and discussion. Interestingly, HR-TEM indicates primary particles being polycrystalline, surrounded by smaller particles. EDX and XAS studies show larger Ni particles, and smaller Co particles around them.

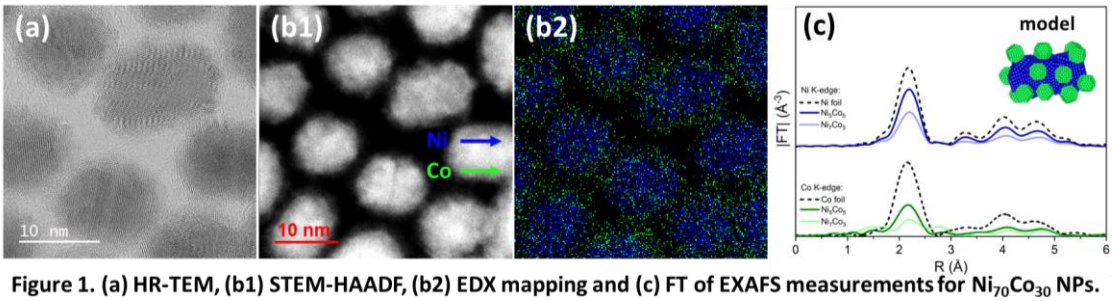

Figure 1. (a) HR-TEM, (b1) STEM-HAADF, (b2) EDX mapping and (c) FT of EXAFS measurements for $Ni_{70}Co_{30}$ NPs.

After catalyst optimization, anisole, guaiacol, and eugenol probed lignin oil upgrading. Additionally, diphenyl ether (DPE), 4-phenoxyphenol (DPE-ol) and monobenzone evaluated C–O cleavage in lignin 4-O-5, α-O-4 and β-O-4 linkages. High conversions and cyclohexanol yields were obtained. Kinetics and application to a realistic lignin model will be disclosed in the conference.

Table 1. Magnetic catalytic performance of $Ni_{70}CO_{30}$ NPs for the hydrogenation of five typical model compounds.

Substrate	Reaction time (h)	Solvent	Conversion	Main products (yield, mol% on carbon basis)
Anisole	8	Decane	*100*	*Cyclohexane (70)*
Eugenol	48	Decane	*100*	*Propylcyclohexanol (83)*
Guaiacol	22	Decane:THF	*61*	*Cyclohexanol (41)*
DPE	8	Decane	*100*	*Cyclohexanol (47); Benzene (34)*
DPE-ol	8	Decane:THF	*46*	*Cyclohexanol (20); Phenol (11)*
Monobenzone	8	Decane:THF	*50*	*Toluene (18) 1,4-cyclohexanediol (15)*

Reaction conditions: 1mmol substrate, 5 mL solvent, 8 mg $Ni_{70}Co_{30}$, AMF 300 kHz (50-100% power), 3 H_2 bar

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Preparation and Stability of Catalysts for Hydrodeoxygenation of Black Liquor HTL-oil

Luděk Meca[1*], Alexey Kurlov[2], Pavel Kukula[1], David Baudouin[2]

[1]*Ranido s.r.o., Praha, Czech Republic*
[2]*Bioenergy and Catalysis Laboratory, PSI, Villigen, Switzerland*
[*]*ludek.meca@ranido.cz*

Keywords: catalyst stability, hydroprocessing, hydrodeoxygenation, black liquor, supercritical water

Introduction. Working on decarbonization of transportation fuels is important for strengthening energy security and sustainable growth. The Black Liquor to Fuel project (BL2F) contributes to that by searching a path from residual biomass – black liquor – to the production of greener fuels. One of the project aims is to develop "Integrated Hydrothermal Liquefaction" process (HTL) converting the black liquor into an intermediate "HTL-oil". Subsequent step to develop – hydrodeoxygenation (HDO) – will allow conversion into a desired fuel intermediate. Herein, we present a study of catalyst stability under a planned operational conditions - supercritical water (SCW) conditions in continuous flow system.

Experimental/methodology. The HDO catalysts compositions containing nickel and molybdenum oxides were impregnated on various supports (Table 1). The supports have been previously tested under SCW conditions [1]. These oxidic catalysts were first sulfided in a batch reactor and their stability under SCW conditions was studied in a continuous flow reactor at 400 °C and 300 bar with a 10 g.min^{-1} flow of H_2O or 1000 ppm dimethyl disulfide (DMDS) in H_2O. The elemental composition of fresh and tested catalysts was determined by SEM-EDX analysis.

Table 1. Properties of the prepared catalysts in oxidic form

Material	Support used for impregnation	BET surface (m^2/g)	XRF composition					
			Al_2O_3 (%)	TiO_2 (%)	$ZrO_2 + HfO_2$ (%)	P_2O_5 (%)	NiO (%)	MoO_3 (%)
BLF-01	α-Al_2O_3	3.5	71	0	0	2.0	3.8	23
BLF-02	rutile (TiO_2)	6.4	0	63	0	2.7	5.9	28
BLF-03	monoclinic ZrO_2	26	0.1	0	66	2.4	5.3	26
BLF-07	activated carbon	759	0	0	0	1.4	4.1	19
BLF-07a	activated carbon	908	0	0	0	0.6	1.3	6.3

Results and discussion. The catalysts in oxidic form have been characterized using XRF, XRD, BET and TEM. The stability of sulfided catalysts was evaluated in a continuous SCW flow and the remaining Mo and Ni content was determined after 2 h on stream. XRD analysis of the tested catalysts showed that in pure SCW flow, Mo is oxidized to MoO_2 and no traces of NiS were observed. The SEM-EDX analysis revealed that more than half of the Mo and Ni was leached out. An additional test of sulfided BLF-07a in a continuous SCW flow containing 1000 ppm DMDS resulted mainly in MoS_2 phase with only traces of MoO_2. That indicated inhibition of MoS_2 oxidation in the presence of sulfur-rich feed. However, the SEM-EDX analysis showed that, similarly to the sulfur-free test, more than 50 % of Mo and Ni was lost during the test. Comparisons of XRD before and after SCW treatment will be presented. Obtained results indicated that NiMo based catalysts were not suitable for applications under SCW conditions.

Acknowledgments
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Hydrodeoxygenation of anisole over Pd/TiO_2 catalyst: pressure-dependent reaction pathways

A. Miró i Rovira[1], K. Ranjerdan[1], P. Tingelstad[1], D. Chen[1*]

[1] *Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Sem Sælands vei 4, 7491, Trondheim, Norway*
[*] *de.chen@ntnu.no*

Keywords: Ansiole, Biomass to fuels, Continuous flow reactor, Hydrodeoxygenation

Introduction. Fast hydropyrolysis (FHP) of biomass is a promising renewable alternative to produce liquid fuels for the transportation industry [1]. However, FHP bio-oil contains a high percentage of oxygenated compounds; thus, chemical upgrading is necessary. An initial stabilization step is performed to stabilize organic acids and other short-chain highly reactive oxygenates present in the bio-oil [2]. Nonetheless, after this initial stage, the bio-oil still has a high oxygen content. Therefore a hydrodeoxygenation (HDO) step, a second upgrading, is carried out. For this step, hydrogen and the bio-oil are pressurized to favor the adsorption of the oxygenates and hydrogen over traditional hydrotreating catalysts to cleave the C-O bond and produce H_2O and hydrocarbons as the desired product [3]. The required high pressure during HDO is the root cause of the main challenges of this process (i.e., high hydrogen consumption in unwanted side reactions, undesired DECOx reactions, and catalyst deactivation). For this reason, catalysts that are capable of selectively deoxygenating phenolic-derivated compounds to aromatics at relatively lower pressures are of great interest. Palladium on titania is reported to exhibit high activity for HDO and selectivity to aromatics [4]. The present work focus on the pressure-dependent reaction pathways in the bifunctional catalyst. The role of both metallic and acid sites and the metal–support interface in pressure-dependent hydrogenation/dehydrogenation reactions and dehydroxylation reactions will be addressed.

Experimental/methodology. The Pd/TiO_2 catalyst was prepared by means of incipient wetness impregnation, and the loading of Palladium was 2% of the total weight of the material. The TiO_2 support was calcined at 400°C for three hours before impregnation. Catalytic testing was performed in a tubular fixed-bed reactor (15 mm inner diameter) at 350°C with a pressure range from 1 to 20 bar. Before the experiment, the catalyst was pretreated under reaction conditions at 400°C. Product analysis was performed by means of GC-MS, for identification, and GC-FID, for quantification of the compounds.

Results and discussion. The product distribution of the different experiments was studied in relevance to the reaction mechanism to understand which was the prevalent main reaction pathway in each scenario. At lower pressures, DECOx reactions gain more dominance over the process, reducing the carbon efficiency (less carbon yield in the liquid product in favor of higher yield of CO and CO_2 in the gas phase). Moreover, some oxygenated saturated species, which are intermediates of side reactions (demethylation + hydrogenation), are not able to be fully deoxygenated, hence retaining the oxygen in the liquid product. On the other hand, at higher pressures, the HDO remains the prevalent reaction pathway. However, excessive hydrogenation to saturated species occurs, and the coke formation increases significantly, both reducing the carbon efficiency and poisoning the catalyst. The pressure is optimized based on a detailed understanding of the pressure-dependent reaction network as a function of the catalyst properties.

Acknowledgments

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Dehydrogenation of 1,4-butanediol over cobalt aluminate synthesized by the sol-gel method, in the presence of different solvents

Gheorghiţa Mitran[1*], Dong-Kyun Seo[2], Octavian Dumitru Pavel[1], Florentina Neaţu[3], Mihaela Florea[1,3]

[1]*University of Bucharest, Bucharest, Romania*
[2]*Arizona State University, Tempe, USA*
[3] *National Institute of Material Physics, Magurele, Romania*
[*]*geta.mitran@chimie.unibuc.ro*

Keywords: cobalt aluminate, 1,4-butanediol, dehydrogenation

Introduction.

Lactones and their derivatives are widespread in nature and very used in industry as extraction agents, solvents, intermediates in pharmaceuticals, petroleum industry and agriculture. γ -Butyrolactone (GBL) is extensively used as solvent and for herbicides, N-methyl-2-pyrrolidone, 2-pyrrolidone, N-vinyl-2-pyrrolidone, polyvinylpyrrolidone production[1]. It can be synthesized by 1,4-butanediol lactonization over cobalt aluminate catalysts[2]. In this study we prepared a series of $CoAl_2O_4$ samples by the sol-gel method, in the presence of water, ethanol, methanol and butanol as solvents, following to establish the relationships between the catalyst properties and the catalytic performances in the lactonization of 1,4-butanediol coupled with acetophenone and benzaldehyde hydrogenation.

Experimental/methodology.

For the catalysts synthesis, sol-gel method has been used using as precursors aluminum isopropoxide $Al[OCH(CH_3)_2]_3$ and cobalt nitrate hexahydrate $Co(NO_3)_2{\cdot}6H_2O$. Water, ethanol, methanol and 1-butanol were used as solvents, while HNO_3 (1M) as hydrolysis rate controller. The obtained gel was dried at 100 ^oC and calcined at 500 ^oC. The microstructure and optical properties were characterized by XRD, SEM, BET, FTIR and UV-VIS techniques.

Results and discussion.

The catalysts prepared in the presence of methanol and butanol as solvents have $CoAl_2O_4$ as the predominant phase, while for the samples prepared in the presence of water and ethanol the predominant phase is Co_3O_4. Ethanol was the effective solvent in sol-gel method, it's using leads to synthesis of the sample with the lower lattice strain, the highest surface Co^{3+}/Co^{2+} ratio and with the highest Co/Al ratio (Table 1). Otherwise, a good correlation of the lactone yield with these parameters was observed for all the studied samples.

Table 1. Structural parameters and specific surface properties of CoAl samples

Sample	D (nm)	BET surface area (m^2/g)	Microstrain (ε) 10^{-3}	Co^{3+}/Co^{2+}	Co/Al
$CoAl_W$	9.8	126	1.70	0.49	1.85
$CoAl_E$	9.9	94	1.62	0.65	1.86
$CoAl_M$	7.9	114	1.98	0.50	1.68
$CoAl_B$	6.6	108	2.39	0.14	1.14

Acknowledgments

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Tuning the Interfaces of Promoted Nickel Catalyst for Hydrodeoxygenation of Palm Oil Towards Biodiesel Production

M. Mohammed[1], S. Alkhoori[1], D. Anjum[1], M.A. Jaoude[1], D. Shetty[1], K. Polychronopolou[1]*

[1] *Khalifa University of Science & Technology, Abu Dhabi, United Arab Emirates*
**Corresponding Author's E-mail address: kyriaki.polychrono@ku.ac.ae*

Keywords: Hydrodeoxygenation (HDO), Zeolite Beta (ZB), Lanthana Promoter, Bimetallic, Ball Milling.

Introduction. Biofuels are promising fossil fuel alternative with a sustainable circular carbon economy [1]. Among the deoxygenation reaction pathways, hydrodeoxygenation (HDO) offers the best prospects for upgrading bio-oil to biofuel without generating pollutants like CO and CO_2 [2]. This study aims to design catalytic systems by investigating the promoter's and mechanochemical treatment's effects on the production of biodiesel through palm oil hydrodeoxygenation reaction.

Experimental/methodology. Catalyst design involved the following approaches: 1) Using a metal oxide promoter to counteract the acidity of the zeolite beta (ZB) support, 2) Synthesizing a bimetallic system (NiCu) to improve metal reducibility and limit coke formation, and 3) Tuning two interfaces using mechanochemical treatment. First, the support is ball milled to decrease the particle size and increase the exterior surface area (***interf-1***). Second, the promoter and support simultaneously ball milled with expected improvement in dispersion and better metal anchoring due to produced defects in the promoter (***interf-2***). *Catalyst synthesis:* Wet impregnation was used to prepare the monometallic (Ni/La-ZB) and bimetallic (NiCu/La-ZB) catalysts. The ZB support used is commercial, from ZEOLYST INTERNATIONAL (SiO_2/Al_2O_3=25). *Post-synthesis treatment:* Interface tuning was achieved using planetary ball milling with water as solvent.

Results and discussion. Various characterization techniques were utilized to study the catalysts' structural and textural properties, surface species, reducibility, and acid/base properties. After investigating the support structure, (XRD) showed that ZB remained crystalline following wet impregnation and post-mechanochemical treatment. An increase in ZB crystal size was seen with the milled *interf-1* catalyst. It increased from 12.08 nm (pristine ZB) to 13.13 nm, attesting to the recrystallization as expected. Additionally, results showed excellent promoter dispersion on the support for all studied catalysts which were apparent in the (XRD) profiles and (HAADF-STEM) images. Moreover, after mechanochemical treatment of *interf-1*, the metal dispersion was further improved and resulted in smaller particles as evidenced by the average crystal size calculated from (XRD) analysis and (HAADF-STEM) images. On the contrary, for *interf-2*, the particles were rather agglomerated. Calculated Ni crystal sizes were 14.49 and 15.36 nm for *interf-1* and *interf-2* (XRD), respectively, and the average metal particle sizes were 33.4 and 44.6 nm (HRTEM), respectively. (H_2-TPR) profiles showed that the addition of Cu greatly influenced the reducibility of NiO, evident in the peaks shifting to lower temperatures. Furthermore, the mechanochemical treatment results showed further peaks shift to lower temperatures attributed to the enhanced metal dispersion and electronic interaction. Incorporating the La promoter increased the basic sites of all the catalysts, as deduced from the (CO_2-TPD) studies performed. (XPS) results showed that the surface Si/Al ratio increased with the addition of the promoter to the monometallic catalyst, indicating changes in the zeolite framework that led to a less acidic surface. (XPS) results also revealed that Cu prefers residing on the surface in all bimetallic catalysts. The next steps of this work involve the continuation of advanced catalyst characterization (NH_3/CO-DRIFTS and Synchrotron XAFS) alongside catalytic evaluation to study the catalyst pathway selectivity and product yield.

Acknowledgments

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Stability analysis of a multi-metallic sample for steam compensated self-reforming of biogas in sulfur presence

E. Poggio-Fraccari*, S. Molina, C. Herrera, M. A. Larrubia, L. Alemany

[1]*University of Malaga, Faculty of Science, Chemical Engineering Department, Malaga, Spain*
[*]*eduardopf@uma.es*

Keywords: biogas, self-reforming, reforming, sulfur

Introduction.

Biogas is an attractive feedstock with financial and environmental benefits as a partial replacement of fossil fuels [1]. An interesting alternative is the conversion of methane by the two simultaneous oxidants naturally present in biogas, CO_2 and H_2O implying a decrease in carbon emissions. If an additional content of steam is introduced by obtaining a $CH_4/H_2O/CO_2$ ratio close to 3/2/1 then, a H_2/CO ratio 2/1 is obtained, which is suitable for most of industrial applications such as methanol production and Fischer Tropchs reaction [2]. However, the main involved is the common presence of sulfur that hinders the raw biogas employment requiring a cleaning treatment and thus increasing the costs of the obtained syngas. A different and cost-effective approach is using a sulfur tolerant catalyst.

Experimental/methodology.

A multi-metallic sample of NiCe with Sn and Rh and supported over high surface alumina was tested in presence of dimethyl sulfide (DMS) at 700 ºC and GHSV: 3200 h^{-1} as it was it was reported elsewhere [3].

Results and discussion.

A long-term run was carried out in presence of two different sulphur contents, Figure 1. The change of poison concentration allowed us to determine if a previously used sample was capable of tolerating this higher concentration. Methane conversion was slightly higher than the corresponding of CO_2 in agreement with the carbon deposition observed and the higher H_2/CO ratio than theoretical expected, 2/1. Additionally, the coke formation and the sulphur content did not conduct a clear deactivation of the tested solid for the firsts 35 hours of run. However, after the switch to a higher poison content, the activity started to decline, taking as much as 25 hours to achieve almost 15% in methane or carbon dioxide conversions. This slow deactivation process might be due to some active sites were firstly passivated by coke deposition after getting contact with more sulphur, preventing a quicker deactivation by previously noticed [3], whilst the closer values of both conversions found imply that another path for CO_2 conversion was simultaneously taken place during the reforming study, probably the reverse Water Gas Shift and the coke gasification by carbon dioxide (reverse of Boudouard reaction) contributing to the noticed decrease of H_2/CO ratio and the increase in carbon balance respectively. The trend found suggests that sulphur deactivation may depend on the previous state of the sample in agreement with some alternatives reported in literature for extending the lifespan of the catalyst like passivation. However, this approach may modify the catalyst performance (activity and selectivity) as it was found in a previous work with the multi-metallic catalyst ex-situ poisoned with DMS [3].

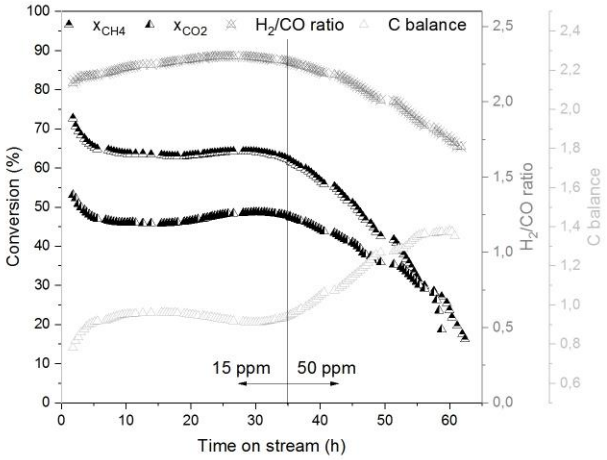

Figure 1. Results of activity test with two different subsequent sulphur contents, 15 ppm followed by 50 ppm.

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Reductive catalytic fractionation of agricultural residues: the case study of Ecuadorian biomass as an attractive source of phenolic monomers

Diego Montesdeoca[1,2*], Damien P. Debecker[1]

[1]*Université catholique de Louvain, Louvain-la-Neuve, Belgium*
[2]*Central University of Ecuador, Quito, Ecuador*
[*]*d.montesdeoca@uclouvain.be*

Introduction.

Current world politics, seeking to reduce the generation of pollutants and solid waste, together with a society less dependant on fossil resources, is driving the search for alternative and sustainable feedstocks for the supply of energy, chemicals and materials.

Lignocellulosic biomass is emerging as a promising alternative to fossil carbon, with streams being especially important in the case of agricultural residues (over 3.3 billion tons per year are generated worldwide[1]), since substantial parts of the crops become waste as straws, husks, cobs, bagasse, and others. This abundant, available and cheap resource could be exploited to produce valuable compounds with potential use as fuels or platform molecules through biorefinery schemes.

Ecuador has an impressive variety of crops and plantations, generating large amounts of biomass which are hardly exploited, so the relevance of treating them whit a lignin-centered biorefinery approach is explored.

At present, reductive catalytic fractionation (RCF), a lignin-first biorefinery approach, is widely studied as a way to depolymerize lignocellulosic biomass into phenolic monomers, leaving the cellulosic fraction almost intact. While woody biomass as feedstock has been prioritized, only scarce information is available concerning less conventional (yet abundant) lignocellulosic biomass sources.

Experimental/methodology.

In this work, the adoption of RCF for the valorization of abundant Ecuadorian agricultural residues is investigated: sugarcane bagasse (SC), banana rachis (BR), rice husks (RH), cocoa pod (CP), guadua cane (GC), hemp stems (HS), and african palm rachis (AP). Typical RCF conditions were applied: 3 g of biomass and 0.3 g of a commercial catalyst (Ru/C, 5 wt%) in 120 mL of solvent (methanol), at 200°C under 30 bar of H_2 (loaded at ambient temperature) for 3 hours. The main process streams (feedstock, lignin oil, and residual pulp) were characterized in depth to gain insights into cellulose and hemicellulose retention in the residual pulp, and especially the fractionation level of lignin into its monomers in the lignin oil.

Results and discussion.

Reductive catalytic fractionation of Ecuadorian biomass derived in residual pulps having delignification degrees in the order of 50% with hemicellulose removals close to 25% and C6 polysaccharides recoveries of about 90%. Also, lignin oils were obtained, whose characterizations revealed the presence of a wide array of lignin monomers, comprising units of propyl-, propanol-, and ethyl-substituted guaiacol/syringol (usual when used woody feedstocks), along with units of methyl-hydrocoumarate/hydroferulate (mirroring the herbaceous nature of the explored biomasses). Also, the unsaturated forms of these monomers were identified. Overall, the phenolic monomer yields followed the order: 26.9% (SC), 15.8% (GC), 15.0% (AP), 13.5% (HS), 9.2% (RH), 6.9% (BR), 1.6% (CP), with more than 67% selectivity for saturated monomers. Notably, hemp stems presented interesting results, since monomers with propanol side chain were obtained with a selectivity ~50% compared to 10-25% shown by the other biomasses. By using another commercial catalyst, Pd/C (5 wt%), used to preserve the OH content of the lignin monomers[2], the selectivity increased to 85% with a total yield of 27%.

On the other hand, agricultural residues showed high contents of ash (4-20%) and extractives (6-36%), when woody feedstocks have less than 1% for ash and below 5% for extractives[3]; we show that high ash contents correlates with low phenolic monomer yields.

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Non-precious transition metal oxide catalysts for the selective oxidation of propylene glycol

Cheslin Moodley[1*], Mzamo L. Shozi[2] and Holger B. Friedrich[3]

[1-3]*University of KwaZulu-Natal, Durban, South Africa*
[*] *214520098@stu.ukzn.ac.za*

Keywords: propylene glycol, selective oxidation, non-precious

Introduction.

An increasing demand for energy, chemical products, food production and the rise in anthropogenic CO_2 emissions worldwide is driving the investigation and development of catalytic processes which replace fossil resources, reduce energy consumption and environmental waste and eliminate the use of toxic and/or hazardous samples [1]. Biomass resources have become widely researched as sustainable and renewable raw materials for producing industrial and fine chemicals, which are in high demand. Upon catalytic transformation of biomass feedstocks (such as glycols, sugars and cellulose), propylene glycol is produced in medium to high yields [2-4]. Thus, due to the presence and functionality of two hydroxyl groups, it presents itself as a candidate starting material for various catalytic transformations, including selective oxidation. Propylene glycol oxidation products such as pyruvic acid, pyruvaldehyde, lactaldehyde and lactic acid have integral roles in the pharmaceutical and agrochemical industries.

Additionally, they have further essential roles in producing fine/speciality chemicals. The C3 acids and aldehydes are currently obtained from routes considered homogeneous (enzymatic), from compounds that are petrochemically derived (for example, propylene) or employ supported precious metal catalysts in batch systems. These routes are considered inefficient, costly and environmentally harmful, which motivates the need for a greener biomass-derived process. This study currently aims to prepare non-precious heterogeneous metal oxide catalysts to be tested in the selective oxidation of propylene glycol.

Experimental/methodology.

CuO and MnOx were supported on MgO, CeO_2 and SiO_2 by wet impregnation. The supports were chosen due to their surface properties, i.e. basic, redox and acidic sites. The catalysts were characterised using surface and bulk techniques such as N_2-physisorption, TGA-DSC, electron microscopy (SEM and TEM), PXRD, and temperature-programmed probing. Catalytic testing was conducted in a continuous flow–fixed bed reactor. The products obtained were analysed using gas and liquid chromatography.

Results and discussion.

CO_2-TPD revealed that the ceria-based catalysts mainly had strong basicity, whereas the MgO-based catalysts ranged in basicity (weak to strong). This difference in basicity is attributed to the presence of basic hydroxyl groups on the surface of MgO compared to CeO_2. These basic sites may play a role in forming acetol which can then be converted to one of the desired products. H_2-TPR was used to assess the extent of reducibility of the prepared catalysts. Reducibility is important as the supported metal oxide has to be reduced in the proposed reaction mechanism to form the desired product. From the results, the copper-based catalysts showed the highest ease of reducibility as they had low temperature (±150 °C) reduction peaks in comparison to the manganese-based catalysts that had multiple higher temperature (>250 °C) reduction peaks. The catalytic testing of the prepared catalysts resulted in various products being formed, including acetol, propanols and lower alcohols. The formation of acetol is promising as it is an intermediate in the production of pyruvaldehyde and pyruvic acid.

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The effect of synthesis method on supported Ni-W catalysts for the hydrogenolysis of erythritol

W. M. Mthiyane[1*], A. Govender[2], M. Shozi[3]

[1,3]*Walter Sisulu University, Mthatha, South Africa*
[2]*Group Technology, Sasol R&T, South Africa*
[3]*University of Kwa-Zulu Natal, Durban, South Africa*
[*]*wmthiyane@wsu.ac.za*

Keywords: synthesis, nickel, erythritol, hydrogenolysis

Introduction. The global community is tasked with coordinating and co-operating to find innovative solutions for clean energy from renewable energy sources. This urgency stems from the detrimental effects traditional ways of harnessing energy from fossil deposits, such as coal, have on the environment and climate. Sugar alcohols, such as erythritol, are profusely oxygenated compounds that present an excellent opportunity for tailored and selective deoxygenation to useful platform chemicals, such as butanediols, through the scission of C-C and C-O bond hydrogenolysis reactions.[1] Catalysts for hydrogenolysis reactions must have the ability to activate hydrogen, one of the key reactants, which is activated over a metal surface. Hydrogenolysis catalysts consisting of a base metal (Ni, Co, Cu *etc.*) promoted by or mixed with a noble metal (Pt, Pd, Rh, Ru, *etc.*) anchored on support materials (alumina, ceria, *etc.*) are critical for the hydrogenolysis of erythritol to useful chemicals.

Experimental/methodology. NiO-WO_x/Al_2O_3 catalysts were synthesized *via* wet impregnation, co-precipitation, and sol-gel methods.[2] Catalysts were calcined and characterized by ICP-OES, PXRD, N_2 physisorption, TPR, SEM and HRTEM, and XPS. The catalysts, reduced only at optimum temperature for NiO → Ni, were tested in a high-pressure autoclave for the hydrogenolysis of erythritol.

Results and discussion. The Ni/Al_2O_3 system facilitates the scission of C-C bonds of sugar alcohol substrates, which is unwanted for our application. The introduction of W not only suppresses the undesired C-C bond breakage through the action of W-oxo species but does this by increasing the active metallic Ni dispersion which gives the Ni-W system potential for selective hydrogenolysis of erythritol to desired products.[3]

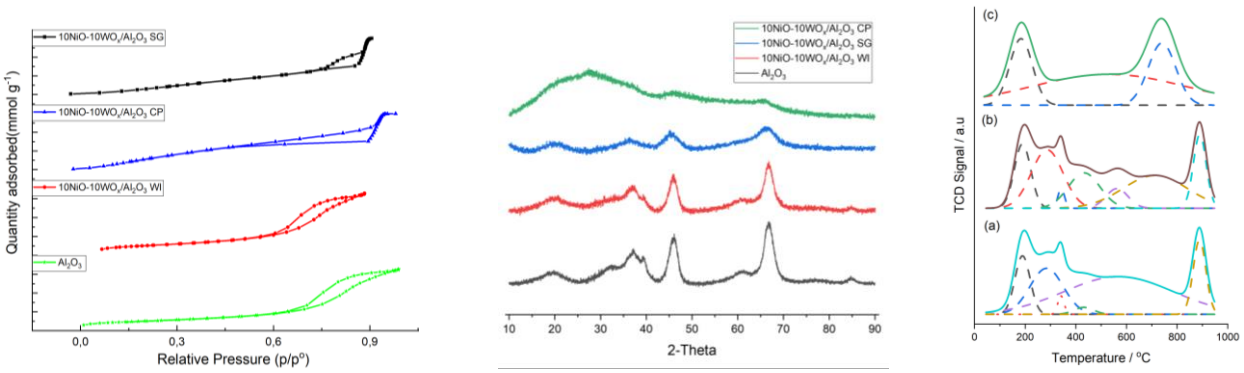

Figure 1: **(a) Type IV N_2 adsorption-desorption isotherms of alumina support and bimetallic catalysts, (b) PXRD of alumina support and bimetallic catalysts and (c) H_2 TPR of bimetallic catalysts (a) 10NiO-10WO_x/Al_2O_3 WI, (b) 10NiO-10WO_x/Al_2O_3 SG and (c) 10NiO-10WO_x/Al_2O_3 CP.**

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Gas phase hydrogenation of crotonaldehyde using formic acid as hydrogen source over Cu and Re supported catalysts

Verónica Naharro[1], C. E. Aristizábal-Alzate[2], M.Romero-Saez[2], I.Rodríguez-Ramos[1], A.B. Dongil*[1]

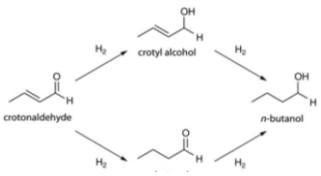
[1]*Grupo de Diseño Molecular de Catalizadores Heterogéneos, Instituto de Catálisis y Petroleoquímica-CSIC, Madrid (Spain)*

[2]*Grupo de Investigación en Química Básica, Aplicada y Ambiente – ALQUIMIA, Facultad de Ciencias Exactas, Instituto Tecnológico Metropolitano, Medellín (Colombia)*

**a.dongil@csic.es*

Keywords: α,β-unsaturated aldehyde, formic acid, copper, rhenium, heterogeneous catalysis.

Introduction. Formic acid (FA) is a renewable biomass material that can be used as a source of hydrogen. FA is a fairly stable molecule, liquid at room temperature, with low toxicity and non-flammable in concentrations below 85% vol. This makes FA decomposition a promising strategy for hydrogen storage abd use. The selectivity is crucial for the production of ultrapure H_2, since the contamination by carbon monoxide produced by the dehydration pathway may reduce the activity of the catalysts [1]. We have previously demonstrated the suitability of FA as hydrogen source for the hydrogenation of gas molecules, butadiene, in the same catalytic bed [2]. In this work we aim at studying the selective hydrogenation of unsaturated aldehydes to unsaturated alcohols using crotonaldehyde (CRO) as a model molecule. This is a challenging reaction since hydrogenation of C=C bonds is easier than C=O bonds thermodynamically and kinetically. With that objective, we have studied Cu and Re as active phase supported on carbon, since they are both active in the FA decomposition and hydrogenation reactions.



Scheme 1. Reaction scheme.

Experimental/methodology. The catalysts were prepared over a commercial high surface area graphite (G, Timcal, S_{BET}: 400 m^2/g) by incipient wetness impregnation using aqueous solutions of NH_4ReO_4 and $Cu(NO_3)_2 3H_2O$ to obtain the same molar loading in monometallic and bimetallic catalysts, eg. 10 wt.% Re for monometallic Re/G. Prior to the reaction, the catalysts were reduced *in situ* at 300 (Cu/G, CuRe/G) or 350°C (Re/G) for 1 h. The gas phase hydrogenation was done in a fixed-bed quartz reactor at atmospheric pressure and 140 °C or 180 °C using fresh catalyst a total flow of CRO 0.42 ml/min and 1.3 ml/min of FA.

Results and discussion. Fig. 1 shows the selectivity and conversion in the hydrogenation of CRO for the evaluated catalysts. At the tested temperatures, FA conversion (not shown) was between 30-90% and selectivity to H_2 98-100%, i.e. the H_2/crotonaldehyde molar ratio was 1-2.8. The results show that it is possible to hydrogenate CRO using FA in the same catalytic bed. The most active catalyst on CRO hydrogenation is that based on Cu metal. However, it is the Re catalyst that achieves highly selective to the target product at both reaction temperatures, i.e. crotyl alcohol, reaching values above those reported by noble metals such as iridium [3]. The effect of temperature was analysed for Re and Cu. As expected, conversion increased with temperature, while the selectivity to propane and butanol increased at the expenses of crotyl alcohol. In contrast, athough Cu is also quite active, it favoured the formation of butanol and butanal. In this tandem catalytic system, selectivity followed a similar trend to that of Cu/G. Further tests are being performed to analyse the effect of using exogenous-H_2 vs FA.

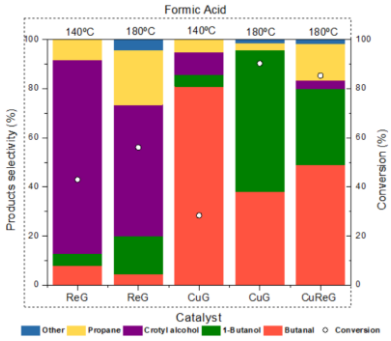


Figure 1. Selectivity (bars) and conversion (circles) using (FA) .

Acknowledgments

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Hydrogenolysis of xylitol to diols over nickel supported on metal oxides

V Ndabankulu*[1], A Govender[2], H.B Friedrich[1] and M Shozi.[1]

[1]*School of Chemistry and Physics, University of KwaZulu-Natal, Durban, 4000, South Africa,*
[2]*Group Technology, Sasol South Africa, Sasolburg, 1974, South Africa*
Owethu.ndabanku@gmail.com

Keywords: nickel, supported catalysts, xylitol, hydrogenolysis, diols

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Introduction

Hydrogenolysis of xylitol produces value-added chemicals such as ethylene glycol (EG), 1,2-propanediol (1,2-PDO), and mono-alcohols such as methanol, ethanol, etc. EG and 1,2-PDO are used in many industrial processes as raw materials in heat-transfer fluid industries, as monomers in the manufacture of polyester resins, and in pharmaceutical, cosmetics, and packaging industries. Generally, the hydrogenolysis of xylitol requires the use of supported metal catalysts (i.e Pt, Ru, Ni, Cu) and the addition of a homogeneous base. Nickel catalysts have been shown to have high activity in the conversion of sorbitol to glycols under high hydrogen pressure and temperature [1, 2]. In this work, we report the performance of Ni and bimetallic Pt-Ni catalysts supported on mixed oxide supports.

Experimental

Metal oxide supports were prepared by the co-precipitation method, using ammonium hydroxide as the base. Calculated quantities of precursor salt solutions were mixed at 60 ^{O}C, pH 10 was maintained, and the temperature of the solution was 80 ^{O}C. The supported catalysts were prepared by the wet impregnation method. Powder x-ray diffraction (XRD) was used to determine the phases in the material. H_2-Temperature programmed reduction (TPR) was used to understand catalyst reducibility. CO_2-Temperature programmed desorption (TPD) was used to quantify the basic sites of the support and catalysts. Xylitol hydrogenolysis reactions were carried out in a high-pressure stainless-steel autoclave.

Results and discussion

N_2 physisorption data showed that all the prepared materials were mesoporous and have a high BET surface area. In all the prepared catalysts Ni was reducible at temperatures below 500 ^{O}C, which meant that the risk of sintering was minimized. Incorporating the base in the alumina structure improved the catalytic activity and selectivity towards glycol at mild reaction conditions.

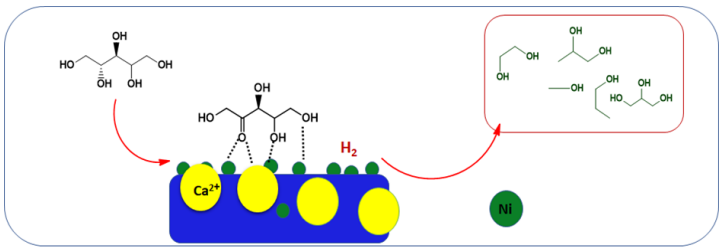

Figure 1. Reaction mechanism for the hydrogenolysis of xylitol over Ni catalyst

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Heterogeneous Catalyst Development for the Hydrogenation of Thermally Unstable Acid-Sensitive Esters

T. Nelis[1], L. P. Manker[1], J. S. Luterbacher[1*]

[1]*Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland*
[*]*jeremy.luterbacher@epfl.ch*

Keywords: Biomass Upgrading, Heterogeneous Catalysis, Hydrogenation

Introduction. Recently, our group demonstrated the direct valorization of hemicellulose into a tricyclic plastic precursor DMGX (Figure 1a), which upon polymerization yielded a new class of degradable, high-performance polyesters.[1] Conversion of DMGX into its corresponding diol, denoted XGDO, could yield a novel rigid structure with promising potential as a bisphenol-A replacement (Figure 1b). However, the selective hydrogenation of esters is challenging due to the low reactivity of the carbonyl group in esters. For this reason, stoichiometric agents such as $LiAlH_4$ are often used. Catalytic hydrogenation using H_2 is an attractive and cleaner alternative, however this generally requires harsh reaction conditions (in industry: 200-300 °C, 100-300 bar H_2), in which the DMGX molecule is not stable. Recent works have demonstrated catalytic systems with milder conditions for hydrogenation of several highly oxygenated, bio-based molecules, but generally utilize specific metal-acid site synergies,[2] which leads to decomposition of the acid-sensitive acetal in DMGX. In addition, another difficulty arises from the DMGX's inherent chemical structure, containing multiple C-O bonds that are prone to metal-catalyzed hydrogenolysis. Here we develop a selective catalytic system for heterogeneous hydrogenation of highly oxygenated, acid-sensitive substrates with low thermal stability, in a green solvent under mild conditions.

Experimental/methodology. DMGX (>99 %) was synthesized as previously reported.[1] Hydrogenations of 0.05-0.1 M solutions of DMGX (in various solvents) were performed in hastelloy Parr reactors (25-50 mL) with metal loadings of 2-8 mol %, 30-50 bar H_2 pressure, reaction temperatures of 150-190 °C, magnetic stirring and reaction times of 12-24 h. The reaction mixtures were analyzed by GC-FID (after silylation) with iso-propylphenol as external standard, and by NMR. Catalysts were prepared via a wet impregnation procedure or commercially obtained. Catalyst supports were self-prepared or obtained commercially.

Results and discussion. Initially, several noble metal catalysts on traditional carbon and oxide supports were screened. These supports led to very complex reaction mixtures with little or no XGDO formation (at high DMGX conversion), indicating the degradation of the cyclic acetal structure in the presence of Brønsted acid sites at elevated temperatures. In order to avoid these sites in the system, weakly-acidic/basic supports such as hydroxy apatite and Mg-spinel were used. Impregnated with ruthenium, these catalysts led to clean reaction mixtures with XGDO yields of up to 47 % (conversion: 98 %, mole balance: 58 %), together with half reduced intermediates, under relatively mild conditions (50 bar H_2 , 190 °C) in cyclopentylmethyl ether (CPME). NMR and GC of the crude reaction mixtures reveal no significant evidence of by-product formation, which when combined with the low mole balance, indicates adsorption of reaction species to the catalyst surface. This is being verified by simple adsorption studies, TGA and catalyst recycling/pre-saturation tests. Finally this system will be evaluated on a larger substrate scope. These results indicate that this system may enable clean hydrogenation of acid-sensitive, thermally unstable oxygenated esters under relatively mild conditions.

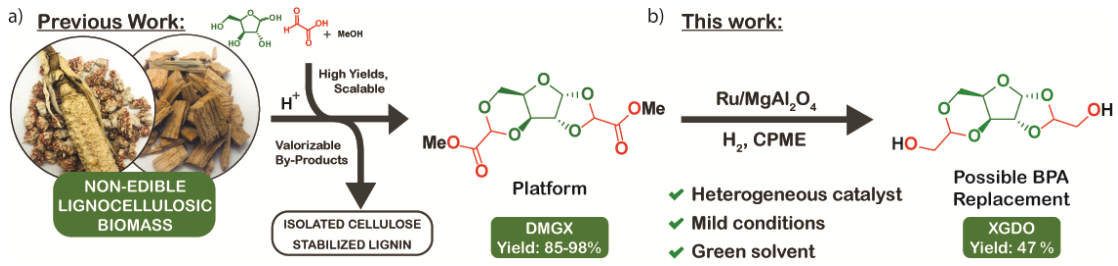

Figure 1. Direct valorization of hemicellulose into DMGX (a) Hydrogenation of DMGX to XGDO (b).

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Understanding the bond functionality for the cascade reaction forming C_2 and C_3 alcohols using nanowires supported catalysts

Ambereen A. Niaze[1*], Aakash Bharadwaj[1],Sreedevi Upadhyayula[1], Mahendra Sunkara[2]

[1] *Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi-110016, India*

[2]*Department of Chemical Engineering, University of Louisville, Louisville, KY 40292, USA*

[*]*ambreen.niazi9@gmail.com (corresponding author)*

Keywords Chemocatalytic, integrated system, ethanol, propane-2-ol, nanowires, tungsten based catalysts

Introduction

The conversion of lignocellulosic biomass into high-value chemicals and fuels, which are currently research hotspots, is a promising technique for reducing energy depletion[1]. The nanowires (NWs) appeared to be very stable, influencing the growing industry and potentially lowering the cost of the process [2]. This work is primarily concerned with the elucidation of reaction mechanisms and the understanding of bond functionality in which the presence of Bronsted acid from tungsten-based catalysts and Bronsted base from hot compressed water (HCW) collectively participate in combination with NWs supported metal catalysts for the conversion of cellulose to C_2 and C_3 alcohols.

Experimental/methodology

Metal oxide nanowires (MNWs) were synthesised using a plasma-assisted method and metal nanoparticles (mP) were impregnated on the as-synthesised NWs. In a high pressure slurry batch reactor, reactions were carried out to obtain the optimal conditions for the desired products, namely C_2 and C_3 alcohols. After performing the series of reactions, the catalysts were characterised to reveal the catalysts-activity relationship. Various analytical techniques were used to quantify the liquid and gaseous products collected after the reactions.

Results and discussion

The as-synthesised MNWs have a tetragonal crystal phase, and the peak at 39.67° corresponds to mP in the PXRD plot shown in Fig. 1. (a). The wire like morphology of mP/MNWs catalysts can be seen in Fig. 1(b) using TEM and SEM at 100nm and 4µm, respectively. The activity performance shown in Fig 1(c) reveals the optimum condition for C_2 and C_3 alcohols. Maximum yields of 32.33% and 51.52% of ethanol and propane-2-ol at optimum condition of R2 and R4, were obtained.

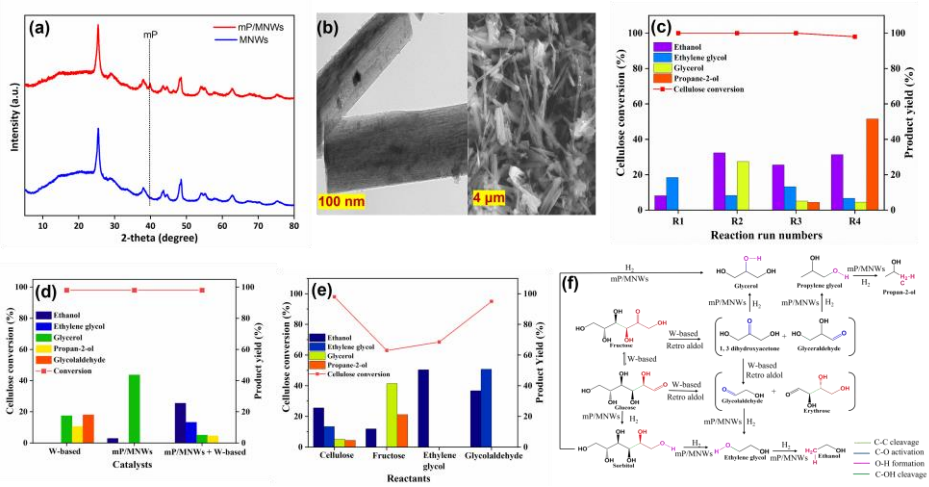

Fig 1. (a) PXRD pattern and (b) morpholoy of pristine catalysts, catalytic activity under various (a) reaction conditions, (d) catalysts (e) reactant (f) bond functionality based on activation and cleavage of bonds

To investigate bond functionality, the reactions were carried out with various catalysts (Fig. 1(d)) and reactants (Fig. 1(e)). These findings suggest that metal sites provide the hydrogenolysis/hydrogenation reaction by forming O-H and cleaving C-OH to form alcoholic products, and tungsten-based catalysts aid in C-C cleavage, allowing the retro aldol reaction to occur, as illustrated in Fig. 1(f).

Acknowledgments

The authors thankfully acknowledge funding support from IITD-HUJI MFIRP (grant no MI02181G).

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High durability of metal-doped Cu/ZnO/Al_2O_3 catalysts in autothermal reforming of model bio-methanol

K. Nomoto[1], H. Miura[1,2,3], T. Shishido[1,2,3*]

[1] *Tokyo Metropolitan University. Tokyo, Japan*
[2] *Research Center for Hydrogen Energy-based Society, Tokyo Metropolitan University. Tokyo, Japan*
[3] *Elements Strategy Initiative for Catalysts and Batteries, Kyoto University. Kyoto, Japan*
[*] *shishido-tetsuya@tmu.ac.jp*

Keywords: Autothermal reforming, Methanol, Lower alcohols, Copper-based bimetallic catalyst.

Introduction. Autothermal reforming (ATR) of methanol is one of the key reactions for on-site hydrogen supply to fuel cells due to its high H/C ratio, low reaction temperature (< 200 °C), and fast start-up operation[1]. Recently, biomass-derived methanol (bio-methanol) has been attracting attention as an alternative to fossil fuel methanol for the realization of a CO_2 recycling system. Generally, bio-methanol contains lower alcohols (0-2%) as impurities[2], which are separated from methanol by energy-intensive purification. In previous work, traces of lower alcohols reduced the catalytic activity and durability of Cu/ZnO/Al_2O_3 (CZA) by depositing carbonaceous species[3]. The inability of the Cu-based catalyst to cleave the C-C bond in lower alcohols was responsible for the inhibitory effect of lower alcohols. In this study, in order to reduce the inhibitory effect of lower alcohols, a series of metal-doped CZA catalysts were prepared and tested for the ATR of methanol with lower alcohols as a model bio-methanol. The effect of metal doping on the catalytic performance was investigated.

Experimental/methodology. CZA was prepared by co-precipitation methods (Cu loading 40 wt%). Metal-doped CZA catalysts (M-CZA: M loading 1 wt%) were prepared by impregnation methods by using CZA as the support. Catalytic tests were carried out in a fixed-bed flow reactor at atmospheric pressure. X-ray absorption spectroscopy (XAS) was performed using the BL01B1 beamline at the SPring-8 (Hyogo, Japan).

Results and discussion. Fig. 1 shows the methanol conversion in ATR of methanol with 1 mol% ethanol at 140 °C. The methanol conversion and hydrogen production rate decreased monotonically with the reaction time for CZA, while they were stable even in the presence of ethanol for Ru-CZA and Rh-CZA. CZA converted ethanol into various C1, C2 and C3 compounds, including methane, acetaldehyde and methyl acetate. On the other hand, the amount of C2 and C3 compounds was significantly reduced, and methane and CO were formed on Ru-CZA and Rh-CZA. Based on the temperature programmed oxidation (TPO) profiles, the carbonaceous species derived from lower alcohols were deposited on CZA, while they were not deposited on Ru-CZA and Rh-CZA. In addition, CZA with ZnO/Al_2O_3(ZA) supported Ru or Rh catalyst (physical mixture) exhibited lower methanol conversion and methane yield than Ru-CZA and Rh-CZA. Structural analysis by XAFS indicated that Cu-Rh and Cu-Ru alloy or Ru oxide were formed. These results suggest that Ru and Rh adjacent to Cu can act as active sites for the decomposition of ethanol and acetaldehyde, resulting in the suppression of carbonaceous species deposition on the Cu surface.

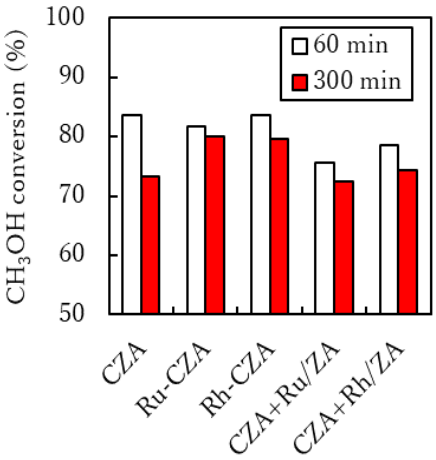

Fig. 1 Time course of methanol conversion with ethanol in ATR at 140 °C. Conditions: Catalyst 100(single), 200(physical mixture) mg, CH_3OH:H_2O:C_2H_5OH:O_2:N_2 =30:36:0.3:10:30 ml min^{-1}.

Acknowledgments

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Gas-phase hydrodeoxygenation of lignin-derived guaiacol and phenol on Ni catalysts using neat and phosphorous-modified γ-alumina supports

Gy. Novodárszki[1*], B. Szabó[1], R. Barthos[1], H. Solt[1], J. Valyon[1], E. Someus[2], D. Deka[3], F. Lónyi[1], M.R. Mihályi[1]

[1]*Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Budapest, Hungary,* [2]*3R-BioPhosphate Ltd., Kajászó, Hungary*
[3]*Biomass Conversion Laboratory, Department of Energy, Tezpur University, Tezpur, India*
**novodarszki.gyula@ttk.hu*

Keywords: guaiacol, phenol, hydrodeoxygenation, Ni/alumina

Introduction. Lignocellulosic biomass is a promising feedstock for the production of renewable chemicals and fuels. Lignin is polymeric component of lignocellulose, comprising of methoxylated phenylpropane monomers. In thermochemical and/or chemical processes, lignin can be converted into liquid products (bio-oils) with a high oxygen content, which mainly consist of aromatic compounds. The oxygen content of bio-oxygenates can be significantly reduced by catalytic hydrodeoxygenation (HDO) reaction [1]. Guaiacol (GUA), a representative component of bio-oil, is commonly used as a model compound in the HDO processes. Products obtained form GUA like cyclohexane (CHN), cyclohexanol (CHL), phenol (PHE), catechol (CAT), benzene (BEN), and toluene (TOL) can be used as fuel, solvent or precursors of nylons, chemicals, polymers, drugs, herbicides, cosmetics, and plastics [2]. The main objective of the present study is the understand the HDO reaction of GUA and PHE model compounds into value-added products. The effect of surface modification and the reaction conditions such as space time, temperature, and pressure as well as time-on-stream on the catalyst activity and selectivity was studied.

Experimental/methodology. Ni catalysts were prepared by wet impregnation using γ-alumina (Al_2O_3, Alfa Aesar) and phosphorous-modified γ-alumina (Al_2O_3(P)) supports. Modification was done with H_3PO_4 solution. The Ni content was 5 and 20 wt%. The catalysts were characterized by XRD, H_2-TPR and FT-IR spectra of adsorbed pyridine and phenol. Catalytic experiments were carried out using a flow-through, tubular, fixed-bed microreactor at 10 bar total pressure in the 200-300 °C temperature range, whereas the space time was varied between 0.1 and 1.0 $g_{cat}\ g_{GUA/PHE}^{-1}$ h.

Results and discussion. Demethylation and transalkylation are the main reactions of GUA over Lewis acid Al_2O_3 and Al_2O_3(P) supports giving CAT derivatives as main products. On 5Ni/Al_2O_3 and 20Ni/Al_2O_3 catalysts, O-free compounds like cycloalkanes and BEN derivatives were mainly formed at 300 °C and 10 bar. At higher temperatures, the thermodynamic equilibrium shifts toward dehydrogenation reaction resulting in mainly BEN derivatives. At lower temperature (225 °C) and/or space time CHL derivatives were also formed in larger quantities. However, Al_2O_3(P) supported Ni catalysts were stable and selective in the formation of PHE derivatives. They catalyze demethylation and demethoxylation but do not initiate ring saturation. In order to clarify the different catalytic behavior, the adsorption complexes formed from PHE chemisorption was investigated by FT-IR spectroscopy. Results show that adsorbed phenolates species are formed on the neat γ-Al_2O_3 support, which is neccessery for further deoxygenation. However, a weak interaction was observed on the Al_2O_3(P) support. Phosphatization was shown to result in partial elimination of Lewis type acid-base pair sites and thereby lowering the surface concentration of phenol intermediates on these sites, which in turn hindered the hydrogenation of the aromatic ring. It was concluded that by using non-noble metal, supported on pure γ-alumina and phosphatized γ-alumina, and adjusting the reaction conditions, the GUA hydroconversion could be directed towards selective formation of required target compound.

Acknowledgments

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Exploring the dehydrogenation behavior of biomass-derived organo-oxygen molecules over MOF and alumina supported platinum catalysts

I. Prieto, J. Gancedo, D. Ursueguía, S. Ordóñez*

[1]*Department of Chemical and Environmental Engineering, University of Oviedo, Oviedo, Spain*
**sordonez@uniovi.es*

Keywords: hydrogen chemical storage, bioplatform molecules upgrading, MOF-supported catalyst, LOHCs

Introduction.

Hydrogen transport and storage is still a bottleneck in the decarbonization of the industrial processes. Chemical storage in unsaturated liquid organics (LOHCs) is a promising alternative for doing these steps in a more safe and economical way. However, these technologies present important challenges to be solved, as the required high selectivities in the hydrogenation and dehydrogenation steps, or the selection of LOHCs of sustainable origin, since most of the LOHCs nowadays proposed are petrochemical derivatives.

In order to propose new LOHCs formulations of renewable origin, the dehydrogenation of the fully hydrogenated forms of biomass-derived molecules has been studied in this work: tetrahydrofuran, representing the hydrogenated form of the furanic derivatives obtained in the hydrolysis of (hemi)cellulosic materials; methyl-cyclohexylketone (MCK) and methyl-cyclohexylether (MCE), representing hydrogenated derivatives of chemicals obtained in the lignin upgrading. Methylcyclohexane (MCH) was used as reference, since toluene/MCH is a typical LOHC nowadays used in industrial practice (Chiyoda Process). As Pt is considered as the most active active phase for these reactions, two Pt catalysts were considered for this purpose, using a common support as alumina and a MOF (MIL-101(Cr)).

Experimental/methodology.

MIL-101 (Cr) was prepared according to literature reported processes[1], Pt being added by incipient wetness[2]. Alumina-supported catalyst was a commercial sample (0.5wt% Pt, Engelhard). Catalysts were tested in a fixed bed reactor (70 mg, 250-350ºC, 0.2 MPa) using a flow of 15 Nml/min with 10 % (mol/mol) of reactant in He. Fresh and used catalysts were characterized for checking the evolution of metal dispersion (HRTEM), morphological changes upon reaction (N_2 physisorption and XRD), and the coke content (TPO).

Results and discussion.

Methylcyclohexane (MCH) present total conversion and selectivity to toluene at T=350ºC for Pt/Al2O3 catalyst. Although selectivity and reactivity trends for MOFs are similar (activation energy of about 84kJ/mol for both catalysts), thermal stability of MOF-supported catalyst is lower. THF dehydrogenation is a more complex reaction, with conversions lower than 27% at 300ºC, and low selectivities to furan, being C3-C4 alkenes the main reaction products. In that case, MOFs-supported catalyst present lower activity. In both cases (MCH and THF) catalyst stability of the MOF-based material is higher, and formation of coke deposits is negligible.

In the case of MCK and MCE, the dehydrogenated products are obtained with higher selectivities (up to 20 % to benzophenone and anisole, respectively), but deactivation effects are also more important with significant formation of carbonaceous deposits. In such cases, the lower acidity of the MOF-based catalysts leads to slighter catalyst deactivation.

Our results suggest that the support can tune the activity of the active phase, as well as the deactivation behavior of the catalyst. Concerning to the molecules, cyclohexylated derivatives are more promising as LOCHs than saturated oxygen heterocycles.

Acknowledgments

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Hydrogenation of nitrobenzene to aniline using various saccharides over titanium(IV) oxide photocatalyst

T. Oto[1,2], K. Ikeuch[1,2], Y. Sakamoto[2], Y. Aono[1,2], A. Onda[1,2], K. Imamura[1,2*]

[1]*Graduate School of Integrated Arts and Sciences, Kochi University, Kochi, 780-8520, Japan*
[2]*Research Laboratory of Hydrothermal Chemistry, Kochi University, Kochi, 780-8520, Japan*
**E-mail: imamura-kazuya@kochi-u.ac.jp*

Keywords: photocatalyst, saccharide, hydrogenation, nitrobenzene

Introduction. The hydrogenation of nitro aromatics to amino aromatics is a very important reaction because amino aromatics are key intermediates for valuable compounds[1]. Generally, the hydrogenation of nitro aromatics is achieved using high-pressure hydrogen gas (H_2) at a high temperature. In addition, industrial H_2 production is steam reforming of natural gas, an exhaustible resource[2]. Therefore, the development of a method with mild conditions for the production of amino aromatics with green H_2 is desired. Since photocatalytic reaction is a redox process caused by photoirradiation under ambient condition, photocatalytic hydrogenation with biomass, renewable resource, has been studied[3]. In this study, photocatalytic hydrogenation of nitrobenzene over TiO_2 using various types of saccharides as an H_2 source was investigated[4].

Experimental/methodology. Bare TiO_2 was suspended in distilled water containing nitrobenzene and glucose in a test tube. The tube was sealed with a rubber septum under Ar and then photoirradiated by a high-pressure mercury arc with magnetic stirring at 298 K. After the reaction, TiO_2 was removed by filtration, and then the amounts of nitrobenzene and aniline were determined by high-performance liquid chromatography with a ODS column.

Results and discussion. Bare TiO_2 photocatalyst almost quantitatively converted nitrobenzene to aniline with various saccharides without the use of hydrogen gas. Although aniline was formed when any saccharide was used, the use of disaccharides (lactose, maltose, and sucrose) decreased the reaction rate. The rate of photocatalytic hydrogenation of nitrobenzene using saccharides is determined by the degradation rate of saccharides at positive holes.

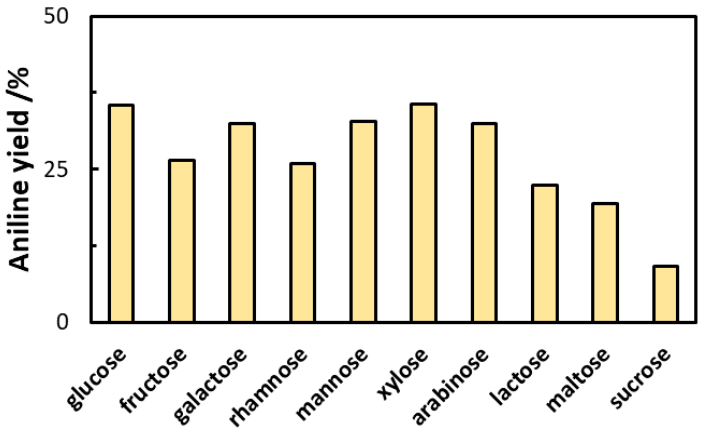

Figure Aniline yield after 60-min photoirradiation in the photocatalytic hydrogenation of nitrobenzene using various saccharides instead of hydrogen.

Acknowledgments
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A Highly Active and Stable Ru Catalyst for Syngas Production via Glycerol Dry Reforming

M. Ozden[1], Z. Say[2,3], Y. Kocak[3], K. E. Ercan[3], A. Jalal[3], E. Ozensoy[3*], A. K. Avci[1**]
[1]*Department of Chemical Engineering, Bogazici University, 34342 Istanbul, Turkey*
[2]*Department of Materials Science and Nanotechnology Engineering, TOBB University of Economics and Technology, Ankara, Turkey*
[3]*Department of Chemistry, Bilkent University, 06800 Ankara, Turkey*
[*]*ozensoy@fen.bilkent.edu.tr*
[**]*avciahme@boun.edu.tr*

Keywords: Glycerol, Carbon dioxide, Dry reforming, Synthesis gas, Ruthenium

Introduction. Problems caused by both of production and consumption of fossil fuels have driven scientists to focus on researching renewable fuel production and effective energy conversion processes. Among these processes, the synthesis of biodiesel from transesterification yields 1 mole of glycerol for every 3 moles of fuel produced. Scientists have proposed different approaches to valorize this excess glycerol. One of these ways is utilizing glycerol as a feedstock for hydrogen and synthesis gas (syngas) production. Until recently steam reforming of glycerol was thoroughly investigated. Another method, which is CO_2 reforming (dry reforming) of glycerol is interesting due to combining two excess compounds into a desirable product. Dry reforming of glycerol is the combination of glycerol decomposition and reverse water gas shift reactions. Due to the endothermic nature of the reforming reactions, if the heating could be done renewably, the dry reforming process can be carbon negative.

Experimental. In this work, dry reforming of glycerol has investigated on Ru/La_2O_3, Ru/ZrO_2, and Ru/La_2O_3-ZrO_2 (support 9 wt.% La_2O_3, all catalysts are loaded with 1 wt.% Ru). Activity experiments were done for 5 hours at 750 °C and a CO_2/glycerol ratio of 1 to 4. Product composition was quantified *via* two on-line gas chromatographs. The effects of the support on catalysts' morphological, electronic, and surface chemistry were investigated thoroughly *via* TEM, *in-situ* DRIFTS, XPS, ATR-IR, and XRD techniques.

Results and discussion. When the activity experiments carried on, Ru/La_2O_3-ZrO_2 have shown the highest CO_2 conversion, which was followed by Ru/ZrO_2 and Ru/La_2O_3. After activity experiments, the stability of the catalysts has been tested in stability experiments at 750 °C and CO_2/glycerol = 3 for 72 hours. In these experiments, Ru/ZrO_2 catalyst was deactivated by 33% due to the sintering of Ru particles, structural deformation of monoclinic zirconia support, and strong metal-support interaction between Ru and zirconia. Under identical conditions, Ru/La_2O_3 catalyst was deactivated by 27% due to severe coking and dehydroxylation/carbonylation of the lanthana support. Lastly, lanthana stabilized tetragonal zirconia support improved fine dispersion of the Ru nanoparticles. Thus, the Ru/La_2O_3-ZrO_2 catalyst deactivated only 15% in the stability experiments, which was on par with more expensive Rh catalysts [2].

Acknowledgments
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Aqueous-phase reforming of black liquor HTL water

J. Palo[1*], M. Reinikainen[1], S. Rautiainen[1], J. Lehtonen[1]

[1]*Technical Research Centre of Finland VTT, Espoo, Finland*
[*]*jasmiina.palo@vtt.fi*

BL2F is a Horizon 2020 project that aims to use pulp mill side-product, black liquor (BL), to produce clean, high-quality fuels for marine and aviation [1]. In the BL2F project, an integrated hydrothermal liquefaction (HTL) process is developed, which includes hydrogen production from black liquor HTL waters via aqueous-phase reforming.

Aqueous-phase reforming (APR) is a catalytic process where oxygenated compounds are converted to hydrogen and light hydrocarbons, typically over a nickel or platinum catalyst [2]. The reaction takes place in aqueous liquid phase at mild temperatures (180 – 250 °C) and elevated pressures (15 – 50 bar) to maintain the feed properties near bubble point. Keeping reactants in the liquid phase also avoids the use of an energetically demanding vaporization step compared to e.g. the steam reforming process. Moreover, hydrogen production is thermodynamically favored at low temperatures with a low carbon monoxide yield. Aforesaid features make APR a promising technology to utilize and upgrade industrial wastewaters.

A limited amount of literature exists on the APR of real process waters, especially in continuous fixed-bed reactors. Therefore, this work focused on testing the APR of HTL process water in continuous operation along with extensive catalyst testing and characterization. Before experiments with real aqueous streams, catalyst screening was carried out with single compounds characterized to be present in the actual feed. MeOH, phenol, and 4-methylcatechol were chosen to represent the main chemical groups to be studied for their characteristic features. Fe- and Ni-based catalysts were synthesized for the experiments and their activities were compared with a commercial Pt catalyst. The hydrogen yield from methanol at the beginning of the reaction was high, up to 40 %, but the catalyst deactivated rapidly in the course of the reaction, Fig 1. The fast deactivation was even more pronounced with the other model compounds. The best catalyst was chosen for long-term operation with real water fraction from the black liquor HTL process. To study the mechanism leading to the fast deactivation, fresh and spent catalysts were characterized with XRD, TOC, ICP, and N_2 physisorption.

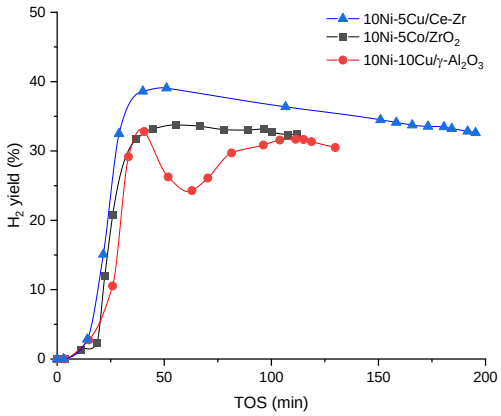

Figure 1. H_2 yield over nickel-based catalysts during APR of methanol. Reaction conditions: T=230 °C, p=32 MPa, Q_{MeOH}= 2 cm^3/min (5 wt-% MeOH in water), and WHSV=4 h^{-1}.

Acknowledgments
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Alkaline Thermal Treatment of Lignin for Sustainable Production of Hydrogen with in-situ Carbon Capture

Jieun Park[1] , Woo-Jae Kim[1*]

[1]*Ewha Womans University, Seoul 03760 (Korea)*
[*]*wjkim1974@ewha.ac.kr*

Keywords: Biomass, Lignin, Alkaline Thermal Treatment(ATT), Hydrogen, CO_2 Capture

Introduction. Biomass is a carbon-neutral energy source that absorbs CO_2 from the atmosphere through photosynthesis and can even be carbon negative when combined with carbon capture technology. Lignin is a natural amorphous three-dimensional polymer that comprises about 30% of lignocellulose biomass and can carry the highest proportion of energy among biomass fractions [1]. In terms of H_2 production from lignin using steam gasification, it produces very low levels of H_2 and high levels of CO_2 and many C_2 hydrocarbon gases. On the other hand, the use of alkaline catalysts can enhance H_2 production from lignin, as we domonstrated with other biomass, such as seaweed. In this presentation, we showed the ATT reaction dramatically increases H_2 production from lignin [2]. NaOH is involved in the production of H_2 and CO_2 capture. It also produces a small amount of CH_4 while inhibiting the evolution of C_2 hydrocarbons and CO_2 [3]. Lignin, a by-product of the waste wood or craft process, has been wided used as a fuel by simple combustion. However, this waste lignin can be made into high value-added energy through the ATT process as we showed in this study.

Experimental/methodology. The reactor consists of a furnace having three temperature zones and a quartz tube. A stoichiometric amount of biomass (lignin) and alkaline catalyst are added to the alumina boat and placed in the middle temperature zone of the furnace. NaOH was used as an alkaline catalyst. N_2 gas was supplied to the Quartz tube as a carrier gas using a mass flow controller. The Agilent 490 Micro GC is used to analyze the product gas collected in the gas tedlar bag and the product gas in real-time.

Results and discussion. The alkaline thermal treatment reaction, in which NaOH is added as a catalyst, introduces a new and simple reaction pathway compared to the existing biomass gasification/pyrolysis, and to convert lignin biomass into hydrogen even at a low temperature. In addition, during the alkaline thermal treatment reaction, carbon from biomass is captured as solid carbonate, and greenhouse gases such as carbon dioxide, which are generated as by-products, are not generated. We produced 83.85 mmol H_2 from 1g of lignin, which is 2 times higher amount of H_2 compared to other biomass ATT.

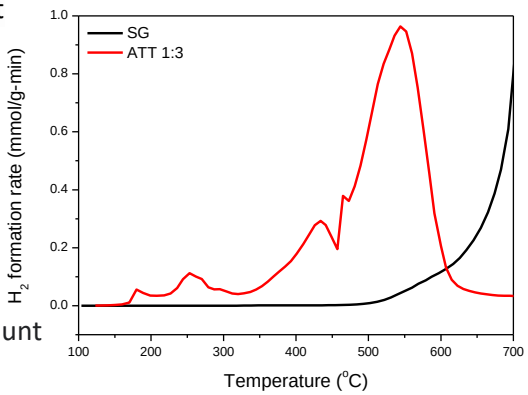

Fig. 1 H_2 production from SG and ATT

Acknowledgments

This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(MSIT). (NRF-2022R1A2C2010744)

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Fabrication of Beeswax/Polypropylene Honeycomb by Using Additive Manufacturing Technique

Jinwon Park[1], Jong Hee Kim[1], Jo Yu Young[2], and Seung Goo Lee[1*]

[1]*Chungnam National University, Daejeon, Republic of Korea*

[2]*National Institute of Agricultural Sciences, Wanju, Republic of Korea*

[*] *lsgoo@cnu.ac.kr*

Keywords: Polypropylene, Additive Manufacturing, Honeycomb, Warpage

Introduction.

Additive Manufacturing(AM) is an open-access technology which allows printing three-dimensional product using various materials with minimal equipment. Fused Deposition Modeling(FDM) type has a high utility and accessibility but has a limit at printing material[1]. Polypropylene(PP) is a industrial material with low cost of production compared to its mechanical strength and chemical resistance, but has a limit to be applied at FDM technique due to its high crystallinity causing warpage and low shape stability[2,3]. In this study PP was composited with beeswax and printed by FDM for the purpose of honeycomb fabrication of beekeeping industry in a streamlined process. PP composites were printed with various printing options to evaluate the warpage and optimize the 3D printer suitability.

Experimental/methodology.

Homo PP was compounded with beeswax, talc, woodflour, compatibilizer and extruded with 1.75mm thickness using a mini filament extruder. Filament PP compounds were printed into 60X60X2mm sized sample using FDM type 3D printer. Printed samples were evaluated its warpage by measuring their length, thickness and distance between sample and surface. Samples were printed with different nozzle temperatures, bed temperatures, and nozzle speeds. The mechanical and thermal properties of PP composites were measured by universal testing machine(UTM), differential scanning calorimetry(DSC), thermogravimetric analysis(TGA). Crystallinity of PP compounds were measured using X-ray differaction(XRD). Also scanning electron microscope(SEM) were used to assess the morphology of printed composites.

Results and discussion.

Warpage data of the PP compound showed that a beeswax contained PP compound has a relatively low shrinking behavior, since the proportion of crystalline region decreased. Containment of beeswax reduced PP composites' warpage behavior but also lowered mechanical strength of compound. Table 1 shows that the absent of compatibilizer cause a least warpage, but slightly reduced the mechanical properties of PP compounds.

Table 1. Mechanical properties of PP compounds

Characterization	ASTM Standard	PP compound	PP/wax	PP/wax/com	Unit
Tensile strength	D638	39.6	31.6	29.0	MPa
Elongation		20	21.2	14.9	%
Flexural modulus	D790	2503	1856	1914	MPa
Flexural Strength		57.3	38.6	36.1	MPa
Izod (@+23°C)	D256	58.8	48.6	38.3	J/m

Acknowledgments

*This reasearch was carried out with the support of the Rularl Development Administration's Agricultural Support Technology Development Project (Project No. PJ016263) *(RS-2021-RD010194)*

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Advanced PbO_2 Anodes for the Bio-based Electrochemical Conversion of Furfural to Maleic Acid

R. Passalacqua[1], S. Abate[1], S. Perathoner[1], G. Centi[1], B. Rawls[2], B. van den Bosch[2]

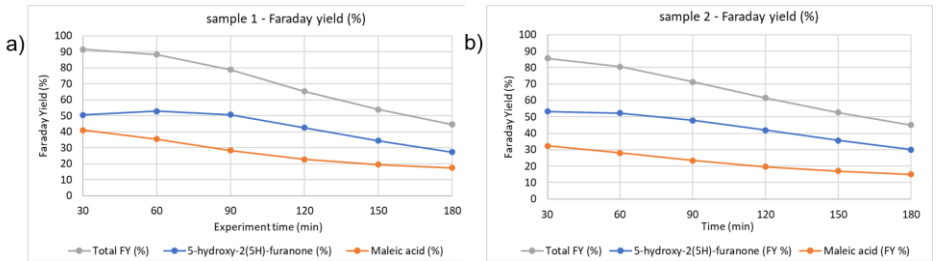
[1] *Department of ChiBioFarAm & INSTM CASPE, University of Messina, Messina, Italy*
[2] *Avantium, Science Park 408, 1098 XH Amsterdam, The Netherlands*
[*] *rpassalacqua@unime.it*

Keywords: electrochemical conversion, PbO_2 anode, furfural, maleic acid, bio-based feedstock

Introduction. Furfural (FF) is a promising renewable platform molecule derived from hemi-cellulose, which can be further converted to various compounds and chemicals, alternatives to the fossil fuel derived ones, thanks to its molecular structure and functional groups. [1,2] Recent advances in the conversion of furfural to maleic acid (MA), and the progress obtained in the development of a PbO_2 based electrode used for setting up a new electrochemical route at industrial scale to produce maleic acid from biobased feedstocks are reported. In particular, the fabrication and characterization of some PbO_2 electrodes, and their electrolysis results obtained conducting the target reaction in a 10 cm^2 lab scale flow cell are presented and discussed.

Experimental/methodology. The electrodes have been prepared starting from different metallic titanium substrates (gauze, mesh). A SnO_2-Sb_2O_3 interlayer was applied, then PbO_2 was deposited by electroplating from aqueous solutions containing Pb^{2+} and Cu^{2+} cations under different conditions. The morphology, crystalline structure, and porosimetry data were collected and investigated whereas oxidation states and surface chemical composition of the electrodes were acquired by X-ray photoelectron spectroscopy (XPS). The samples were tested as anode for the reaction of FF → MA in a microflow divided cell (ElectroCell) using 0.5 M H_2SO_4 and 75 mM furfural (100 mL) as catholyte. A Pt gauze was the cathode whereas Nafion 324 CEM served as cell membrane. 3-hour experiments were carried out sampling every 30 minutes and analyzing the obtained products. The results were expressed as combined Faraday yield (FY maleic acid + HFO) where HFO denotes the 6-electron reduction intermediate of the reaction.

Results and discussion. Stringent control of electroplating conditions of parameters such as temperature and current density is necessary to obtain the β-PbO_2 active in the reaction. An inner SnO_2-Sb_2O_3 layer prepared by dip-coating and thermal decomposition method ensures a good adhesion of the PbO_2 electrodeposited coating with a cheap and affordable procedure that allow to obtain a stable DSA having the requirements for industrial application. Improved performances were obtained using PVA to modify the PbO_2 electrode deposition, as shown from the electrochemical testing results reported in figure below. The chemical-physical characterization of the anodic materials prepared and tested together with the electrochemical investigations were useful to identify the key parameters that determine the performance of the electrode and helped to direct the choices for its optimization in view of the subsequent scaling up.



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Valorization of light bio-oxygenates via ketonization and condensation: definition of reaction pathways and kinetics on TiO_2

V. Piazza[1], C. Gambaro[2], L. Lietti[1], A. Beretta[1*]

[1]*Laboratory of Catalysis and Catalytic Processes, Politecnico di Milano, Milan, Italy*
[2]*ENI– Novara Laboratories (CENTR), Novara, Italy*
[*]*alessandra.beretta@polimi.it*

Keywords: ketonization, aldol condensation, TiO_2, bio-oxygenates, bio-fuels

Introduction. The development of a catalytic system for the conversion of light oxygenates (i.e. C_2-C_4 carboxylic acids, ketones, aldehydes, alcohols) via chain-growth reactions represents an attracting strategy to enrich pyrolysis bio-oil with valuable compounds for fuel and chemical applications [1]. In this respect, C-C coupling reactions like ketonization and aldol condensation can transform light bio-oxygenates into species with longer C-chain and lower O-content, thus enhancing their stability and heating value. Unveiling reaction pathways and kinetics is of the utmost importance for mechanism comprehension and catalysts screening, as well as to tune process selectivities and foster catalyst stability. In this work, the reactivity of two model oxygenates (acetic acid and acetone) on TiO_2-based catalysts was investigated.

Experimental/methodology. Ketonization and aldol condensation tests were carried out in an isothermal micro fixed-bed reactor, feeding acetic acid or acetone, respectively. A commercial anatase TiO_2 powder (Tronox, DT-51D) was used (140-200 mesh), after calcination in air at 400°C and pre-treatment in H_2 at 400°C. Experiments were performed at varying temperature (150-400°C), GHSV (2-6·10^4 NL/h/kg) and inlet concentration of the reacting oxygenate (1.5–3.5 % in He/N_2). Online measurements in a GC-TCD (Agilent 6890) were used to analyze the composition at the inlet and the outlet of the reactor, and were coupled to offline GC-MS analyses (Agilent 6890, 5973 MSD) for species identification.

Results and discussion. Tests with acetic acid limited to temperatures below 300°C allowed to selectively activate ketonization reaction to acetone ($2CH_3COOH \rightarrow CH_3COCH_3 + CO_2 + H_2O$), revealing a wide coverage of catalyst active sites and a zeroth order dependence [2]. At higher temperatures, the appearance of several heavier compounds ($C_{6\text{-}10}$) showed an increased complexity of reaction network with the ignition of secondary reactions starting from acetone. Experiments feeding acetone as reactant were performed to observe the impact of changing operating conditions on products distribution. As an example, the effect of reaction temperature is shown in Figure 1, where the main products are seen: C_6 oxygenates (MO mesityl oxide, MIBK methyl isobutyl ketone), isophorone (cyclical oxygenated C_9), mesitylene (deoxygenated aromatic C_{9_deoxy}) as well as C_4-C_7-C_{10} olefins. The complex variety of products composition reflects the existence of multiple reaction routes, among which emerge consecutive acetone condensations ($C_3 \rightarrow C_6 \rightarrow C_{9\_deoxy}$ or $C_3 \rightarrow C_6 \rightarrow C_9 \rightarrow C_{9\_deoxy}$) and competitive cracking to olefins. Experimental data are now exploited to define a reaction scheme and to quantify kinetics. Moreover, broad catalyst characterization (BET, XRD, TPR, $CO_2/NH_3/CH_3COOH$-TPD) allowed to associate activity values to catalyst morphology and features, while analyses on spent catalytic samples (BET, TPO) revealed a decreased pore volume due to the build-up of C-deposits.

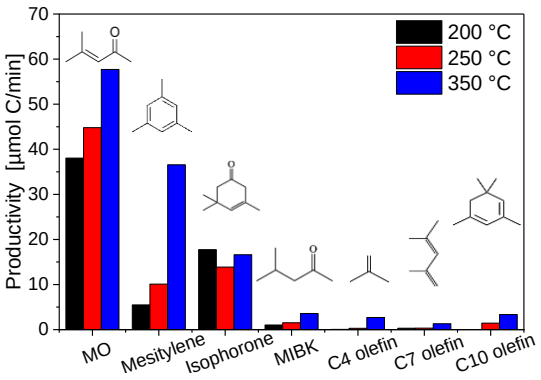

Figure 1. Productivity of main C-products during acetone condensation at varying temperature. GHSV=4·10^4 NL/h/kg_{cat} (total 4600 µmol/min). Feed: 3% acetone in He/N_2.

Guided by the ongoing kinetic analysis, strategies to control process selectivity and to hinder the production of undesired products with C-coking tendency (e.g. olefins) are under investigation.

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Tuning selectivity in carbohydrates conversion with Lewis-acidic zeolites

Yacine Boudjema*, Gerhard Pirngruber, , Mickael Rivallan, Emmanuel Soyer, Céline Chizallet, Kim Larmier

IFP Energies nouvelles, Rond-point de l'échangeur de Solaize – BP 3 69360 Solaize, France

yacine.boudjema@ifpen.fr

Introduction. Carbohydrates such as glucose, fructose or xylose can be transformed to obtain valuable products, such as furanic compounds and organic acids. Nevertheless, the catalytic processes involve a complex reaction scheme, and the selectivity strongly depends on the substrate and on the catalyst. Zeolites with transition metals in the structure, especially Sn-BETA, have shown good activity for glucose isomerization. However, while the specific case of glucose isomerization on Sn-BETA is mechanistically understood[1], the other reaction pathways such as retro-aldolization, dehydration to organic acids have been less well elucidated. Likewise, the influence of different Lewis acidic sites (metals) or of the substrate (sugar) has been scarcely examined so far. Herein, we study the selectivity of the reactions of transformation of biomass-based carbohydrates over different Lewis acidic zeolites.

Experimental/methodology. A commercial beta zeolite was dealuminated by a strong acid (HNO_3 69%). Once dealuminated, Sn, W, Zr or Hf were incorporated (precursors: $SnCl_4{\cdot}5H_2O$; $ZrOCl_2{\cdot}8H_2O$, $W(C_{12}H_{30}O_6)$; $HfCl_4$) targeting a content of 1% wt. Solid State Ion Exchange (SSIE) and Equilibrium Adsorption in a solvent (water or isopropanol, EAW or EAI, respectively) were compared. Pyridine adsorption monitored by in situ FTIR allowed probing Lewis acid sites. The reactivity of glucose, fructose and xylose was studied and compared at two different temperatures (95 °C and 150 °C) in aqueous medium (40 bar N_2).

Results and discussion. The dealumination treatment decreased the aluminum content in the parent material from Si/Al =13 to about 200 with no structural or textural modification. In the case of Sn and Hf, we found incorporation methods allowing the deposition of the targeted amount of metal in the zeolite, without forming metal oxide clusters. For these two metals, the Lewis acidity measured by pyridine was perfectly correlated to the amount of deposited metal. In the case of Zr and W, however, the formation of metal oxide clusters could, for the moment, not be avoided. Further work needs to be done on the preparation protocol for these two metals. In the catalytic tests, Sn-BETA selectively converts glucose into fructose. Little-to-no selectivity towards retro-aldolization of glucose was observed. On the opposite, the conversion of fructose and xylose led to significant rates of formation of retro-aldolization products with Sn-BETA. The formation of lactic acid is also observed with these substrates. A correlation between catalyst activity and Lewis acid site concentration is noticed with Sn-BETA. However, Hf-BETA and Zr-BETA are almost inactive, in spite of the presence of Lewis acid sites. Thus, not only the amount of Lewis acid sites matters, their quality is important. The W-incorporated materials yield mannose in the conversion of glucose (epimerization product), but we observed a near total leaching of the metal in solution during the reaction. This study reveals that the metal could drive the reaction selectivity.

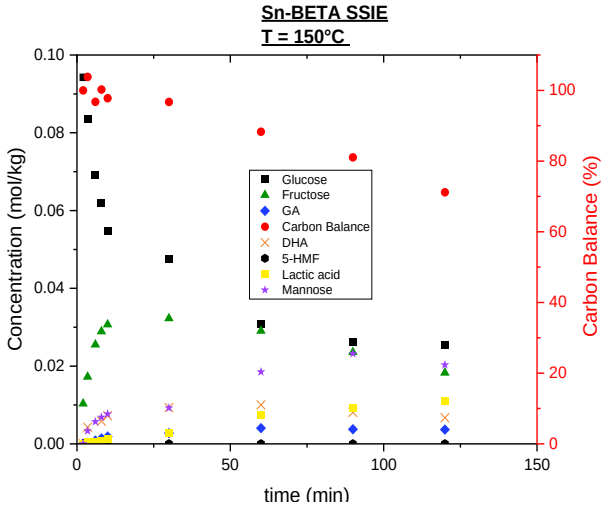

Figure 1: Glucose conversion versus time over Sn-BETA SSIE. Reaction conditions: T= 150 °C, P= 40 bar N_2, initial concentration of glucose 0.1 mol/kg and $n_{metal}/n_{substrate}$= 1/100

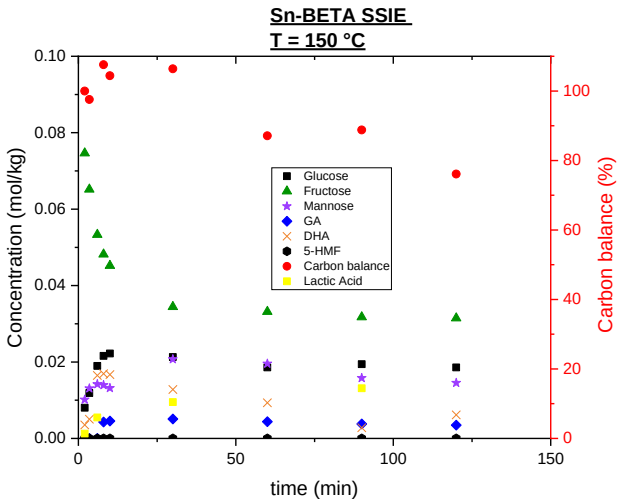

Figure 2: Fructose conversion versus time over Sn-BETA SSIE. Reaction conditions: T= 150 °C, P= 40 bar N_2, initial concentration of fructose 0.1 mol/kg and $n_{metal}/n_{substrate}$= 1/100

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Ethanol dehydrogenation over Cu/SiO_2 catalysts prepared by sol-gel, impregnation, and deposition techniques: The effect of Ni and Zn doping

T. Pokorny[1], V. Vykoukal[1], P. Machac[1], N. Scotti[2], Z. Moravec[1], A. Styskalik[1*]

[1]*Department of Chemistry, Masaryk University, Brno, Czech Republic*
[2]*CNR-SCIETEC, Milano, Italy*
[*]*Corresponding Author: styskalik@chemi.muni.cz*

Keywords: Ethanol, Copper nanoparticles, Acetaldehyde, Sol-gel method, Impregnation method

Introduction. Copper in the form of nanoparticles (NPs) is a well-known redox catalyst active in numerous catalytic reactions, including ethanol dehydrogenation to acetaldehyde. This reaction is critical for the future due to the ongoing changes in the oil industry: ethanol dehydrogenation is the first step of possible sustainable production of butadiene from bioethanol. Cu NPs deposited on silica used for this purpose suffer from low stability during time-on-stream due to the nanoparticles' sintering and coking.[1] Therefore, we have studied particle size and doping effects of Cu/SiO_2 catalysts to improve their stability.[2]

Experimental/methodology. This work is focused on the preparation of SiO_2-supported nanoparticles (Cu/SiO_2; 2.5 wt%; commercial Aerosil-300 used as catalyst support) by several methods to control the nanoparticles size: dry impregnation, strong electrostatic adsorption[3], sol-gel method[4], and deposition of pre-prepared NPs by solvothermal hot-injection synthesis.[5] Catalysts with leading performance were doped with Ni and Zn (Cu:M ratio: 10:1 and 100:1 wt%) by dry impregnation. The catalysts were characterised by STEM-EDS, N_2 porosimetry, TGA, TPR, ICP-OES, and XPS. The catalytic activity of prepared Cu/SiO_2 was tested in a gas-flow fixed-bed reactor connected to gas chromatograph. Sintering of nanoparticles was evaluated by STEM-EDS and coking by XPS and TGA after the catalytic tests.

Results and discussion. The largest particles were prepared by solvothermal synthesis (14.7 nm). Dry impregnation caused a broad distribution of particle sizes (3.9 nm) compared to the narrow distribution by strong electrostatic adsorption (2.6 nm). The smallest NPs were prepared by hydrolytic and non-nonhydrolytic sol-gel (mostly atomic clusters). All Cu/SiO_2 catalysts were highly selective to acetaldehyde (>90 %). The catalysts prepared by hydrolytic sol-gel and dry impregnation exhibited outstanding performance at 255 °C (65 % ethanol conversion and 2.79 g g^{-1} h^{-1} acetaldehyde productivity and 57 % of ethanol conversion and 2.42 g g^{-1} h^{-1} acetaldehyde productivity, respectively). All catalysts suffered from the sintering (**Fig. 1**) and coking above 255 °C causing a severe deactivation. The most stable catalyst (dry impregnation) stabilized at 50 % ethanol conversion after 14 hours time-on-stream. Doping the most active (hydrolytic sol-gel) and the most stable (dry impregnation) catalysts with Ni and Zn led to the following results: (i) Nickel enhanced the catalytic activity at 220 °C but caused a strong deactivation at higher temperatures; (ii) Zn-doped catalysts exhibited better stability up to 290 °C without losing both activity and selectivity.

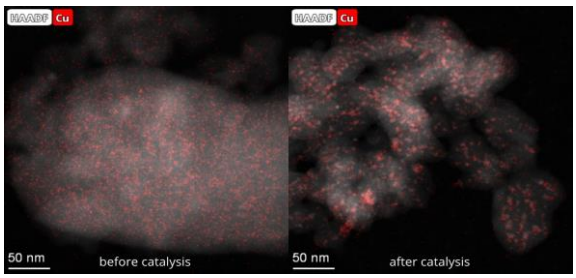

Figure 1: Sintering of Cu nanoparticles (red color) followed by STEM-EDS.

Acknowledgements
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Effect of pore-opened nanosized Cu-MOR zeolite in catalytic dehydrogenation of ethanol to acetaldehyde

A. Prasertsab[1], P. Chaipornchalerm[1], P. ladrat[1], C. Wattanakit[1]*

[1]*Department of Chemical and Biomolecular Engineering, School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand*
**Corresponding author: chularat.w@vistec.ac.th*

Introduction. Ethanol conversion is one of the promising alternative routes for the production of versatile chemicals, for example, acetic acid, ethylene, acetaldehyde, and diethyl ether. Among them, acetaldehyde is one of the vital chemicals to produce several industrial substrates, such as drugs, perfumes, and disinfectants. However, acetaldehyde production via the oxidative dehydrogenation still suffers because it requires the addition of oxygen under high temperatures, high production cost, and unfriendly environmental conditions. Therefore, non-oxidative dehydrogenation of ethanol to acetaldehyde is considered to be an alternative route. Indeed, several catalysts including metal oxides, zeolite, and mesoporous silica combined with noble metal active sites have been applied as promising catalysts. Although they performed high ethanol conversion, low acetaldehyde yield was obtained. In this contribution, we fabricated nanosized Cu-based mordenite (MOR) zeolites with their pore-opened structures for ethanol conversion to acetaldehyde. The generation of secondary pores of zeolite was obtained using the ammonium fluoride (NH_4F) etching approach, which could significantly enhance the accessibility to active sites. In addition, the effect of different types of mesoporous structures on the catalytic activity was systematically investigated.

Experimental/methodology. The nanosized MOR zeolite was synthesized via a simple hydrothermal method using nano-silica as a silica precursor. Subsequently, the pore-opened MOR was prepared by etching the obtained nanosized MOR with NH_4F solution. Afterwards, the Cu-MOR was prepared via the ion-exchange method using Cu aqueous solution at the optimized conditions. The catalytic performance of dehydrogenation of ethanol to acetaldehyde was investigated using a fixed-bed reactor at 300-450°C. The reaction mixtures were analyzed using gas chromatography (GC) equipped with an FID detector and PoraBOND Q column.

Results and discussion. We reported here the catalytic performance of ethanol dehydrogenation to acetaldehyde over Cu-based nanosized MOR as displayed in Figure 1. It was found that the unmodified Cu-MOR with 4.5 wt% of Cu (4.5wt%Cu-MOR) provides 67% of ethanol conversion and 50% acetaldehyde yield. Surprisingly, the pore-opened nanosized Cu-MOR (4.5wt%Cu-NH_4F-MOR) can greatly improve the catalytic performance, eventually achieving high ethanol conversion (85%) and acetaldehyde yield of 57%. This work highlights new possibilities for acetaldehyde production from ethanol using the modified nanosized MOR catalyst.

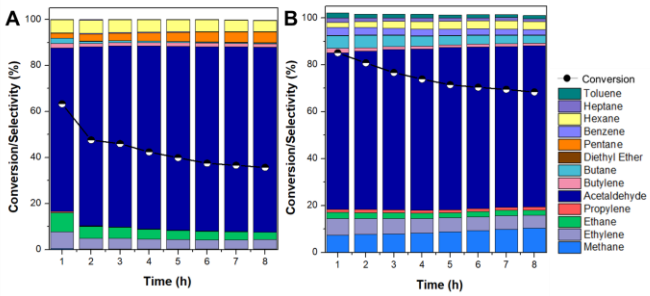

Figure 1. Catalytic performances of (A) 4.5wt%Cu-MOR and (B) 4.5wt%Cu-NH_4F-MOR in the dehydrogenation of ethanol to acetaldehyde under the optimized conditions.

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Acknowledgement

Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong 21210, Thailand
PTT Exploration and Production Public Company Limited, Bangkok 10900, Thailand

Properties and performance in transesterification of potassium catalysts on zeolite X prepared by impregnation and physical mixing

P. Tayraukham[1], K. Deekamwong[1,2], C. Keawkumay[1,2], J. Wittayakun[1], S. Prayoonpokarach[1*]

[1]*School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, Thailand*
[2]*Institute of Research and Development, Suranaree University of Technology, Nakhon Ratchasima, Thailand*

Keywords: potassium catalyst, zeolite NaX, impregnation, physical mixing, transesterification

Introduction. Potassium supported on zeolite NaX (K/NaX) has been used as a catalyst for transesterification to produce biodiesel [1,2]. The catalyst is prepared by the impregnation (IM) method [1,2] by adding CH_3COOK in buffer solution on zeolite NaX. K_2CO_3 is generated after calcination and is believed to be the active catalytic site [1,2] . However, the IM method is time-consuming and involves several steps. This work investigates an approach to reduce the catalyst preparation time by using the physical mixing (PM) method. The properties and performance of IM and PM catalysts are compared.

Experimental/methodology. K/NaX from the IM method was prepared by impregnation with a method from the literature[3]. Potassium acetate buffer was a precursor and the potassium loading was 12 wt%. The sample is named IM. K/NaX from the PM method was prepared by grinding NaX powder and CH_3COOK for 20 min. The sample is named PM. The IM and PM sample after calcination at 500 °C for 3 h are named IMC and PMC. The samples were characterized by TGA, XRD and FTIR and tested in transesterification of palm oil with the method from the literature [3]. The products were analyzed by thin-layer chromatography and gas chromatography.

Results and discussion. TGA thermograms of NaX, IM and PM show weight loss below 350 °C from the adsorbed water (Figure (a). The amount of weight loss was in the order NaX > PM > IM. IM and PM show weight loss in the range of 400 – 460 °C, corresponding to the decomposition of CH_3COOK to generate K_2CO_3 [6,7]. Therefore, calcination at 500 °C is suitable for generating K_2CO_3 as active species. XRD patterns of all samples show characteristics of zeolite NaX and the intensity decreased after calcination. FTIR confirmed the presence of carbonate species on NaX. Figure (b) shows gas chromatograms of the biodiesel products. The biodiesel yield of NaX was null, whereas those from IMC and PMC were 55.3% and 45.5%, respectively. It can be concluded that the dispersion of potassium species on zeolite NaX by IM method enhances the catalytic activity compared to the PM method.

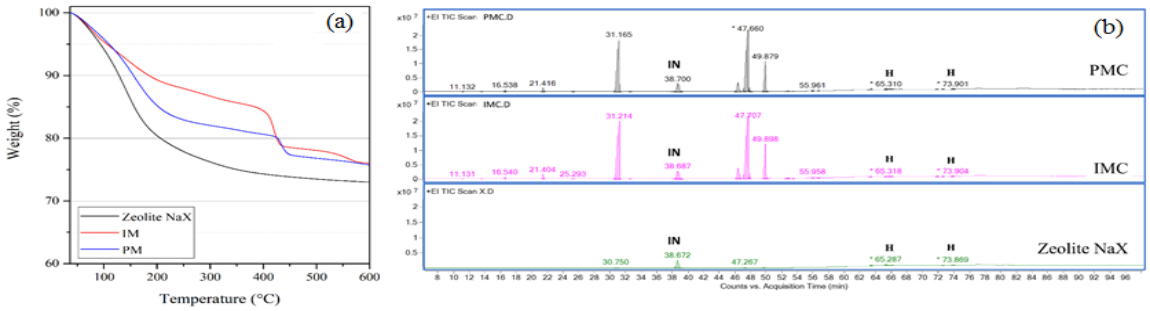

Figure (a) TGA (b) GC results from transesterification products from zeolite NaX, IMC and PMC.

Acknowledgments

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Gas phase dehydration of tetrahydrofurfuryl alcohol into dihydropyran over sol-gel Al_2O_3-TiO_2 catalysts: *In-situ* DRIFT reaction monitoring.

J.A. Pulido[1*], F. Vila[1], D. M. Alonso[1], M. López Granados[1], R. Mariscal[1]

[1]*Institute of Catalysis and Petrochemistry (ICP-CSIC), Madrid, Spain*
[*]*ja.pulido@csic.es*

Introduction. 1,5-pentanediol (1,5-PDO) is a high-value product due to its multiple applications [1]. The production of 1,5-PDO from petroleum derivatives is costly because it involves complex steps and C_5 feedstocks are not available on a large scale. In contrast, there are C_5 feedstocks obtained from biomass, such as furfural (FUR), which is produced on an industrial scale. Among the green routes to produce 1,5-PDO from FUR, the most competitive is the Dehydration-Hydration-Hydrogenation (DHH) multistep route because it employs cheap catalysts resulting in high yields [2]. An essential step is the gas-phase dehydration of tetrahydrofurfuryl alcohol (THFA) to give rise to dihydropyran (DHP). To date, the ideal conditions for such reaction have been reported by [2], who obtained DHP yields of 86% employing γ-Al_2O_3 as catalyst at 375°C in a continuous flow reactor. This work aims to lower the temperature of this reaction by using acid catalysts based on Al_2O_3-TiO_2 mixed oxides to obtain 1,5-PDO from biomass more competitively.

Experimental/methodology. Five acid catalysts were studied; pure oxides (Al_2O_3 and TiO_2) were purchased, whereas three Al_2O_3-TiO_2 mixes oxides have been synthesized by sol-gel method [3] and labeled as SG_2(Al_2O_3)(TiO_2), SG_(Al_2O_3)(TiO_2), and SG_(Al_2O_3)2(TiO_2). The dehydration reaction of THFA into DHP has been followed by in situ monitoring infrared spectroscopy at 200°C and 400°C.

Results and discussion. Figure 1 shows the spectra obtained for five catalysts just before cutting the THFA feed (19,5 min). The infrared bands observed at 2973 and 2875 cm^{-1} are associated with the presence of THFA on the catalyst surface, while the peaks at 1597 and 1463 cm^{-1} can be associated with the formation of DHP. Therefore, the main inference is that the mixed sol-gel catalysts, unlike the commercial catalysts, show activity at 200°C. Specifically based on DRIFT spectra, the SG_(Al_2O_3)(TiO_2) catalyst presents the best behavior on the THFA conversion and DHP yield. When these experiments were conducted at 400°C, all the samples were active in the THFA dehydration reaction. This behavior is due to the different surface acidity of the catalysts, determined by DRIFT after adsorption of pyridine and deuterated acetonitrile as probe molecules.

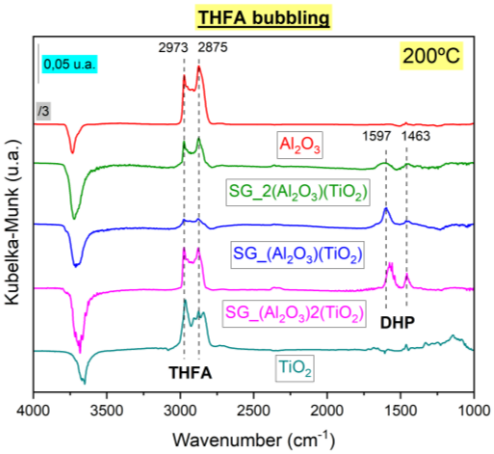

Figure 1. DRIFT *in-situ* spectra monitoring for the Al_2O_3-TiO_2 acid catalysts.

In conclusion, *in situ* monitoring of the reaction may allow us to detect intermediates and deactivation species on the surface, in addition to reactants and products. The previous results are promising regarding the use of Al_2O_3-TiO_2 mixed catalysts to lower the dehydration temperature of THFA to obtain DHP.

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Two-step configuration of carbon-carbon coupling and hydrodeoxygenation catalyst for the upgradation of biomass derived oxygenates

Kishore Rajendran[1], Albert Miró i Rovira, Petter Tingelstad, Kumar R. Rout[1], De Chen[1*]

[1]Dep. of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway
Email: de.chen@ntnu.no

Introduction. Biomass valorization in the transportation sector is highly anticipated due to the increasing demand for green fuels. Predominant literature in Hydrodeoxygenation (HDO) is directed toward the reduction of oxygen species. The carbon yield of liquid fuels is critical for energy efficiency and the cost of biomass conversion [1]. However, only limited focus is given to the simultaneous retention of carbon together with the removal of oxygen species in the final upgraded bio-fuel to increase the carbon yield. The C1-C5 short-chain oxygenates (ketones, aldehydes, acids) represent 15-20% of the conventional bio-oil obtained via fast-pyrolysis. The unstabilized bio-oil poses challenges such as its acidic nature, low H/C, high O/C ratio etc., which are not compatible with current gasoline/diesel range fuel specifications [2]. Therefore, a two-step configuration of carbon-carbon (C-C) coupling and HDO catalyst could potentially convert under-utilized short-chain oxygenates into long-chain oxygenated hydrocarbon, which could be further deoxygenated by the HDO catalyst.

In this work, hydrogenation metals such as Au, Cu, Ni, Ru, Pt, and Pd were supported on reducible oxides such as TiO_2, ZrO_2, CeO_2 for C-C coupling upgradation. Coupling the assessed C-C coupling reaction using real biomass feedstock (beech wood) was later combined with HDO catalysts such as Mo, Nb, Re, W supported on TiO_2 support.

Experimental/methodology. Two fixed-bed stainless-steel reactors were used in series to perform pyrolysis at 600 °C and followed by ex-situ catalytic upgradation at 300-400 °C, 1 bar. The C-C coupling catalyst was placed prior to the HDO catalyst in the 2nd reactor. The gaseous products were analyzed by GC-TCD/FID, whereas liquid products were analyzed by GC-MS/FID. The water content of the bio-oil was analyzed by Karl Fischer titrator.

Results and discussion. We observe Cu and Au to outperform other strong hydrogenation metals during C-C coupling reaction. On the other hand, the combination of Mo-Nb, Re-Mo over TiO_2 support showed superior activity compared to other candidates for HDO catalysts. Overall, the dual-bed configuration was successfully implemented to retain higher carbon in the upgraded bio-oil with decreased oxygen content compared to conventional HDO treatement. Additionally, all the synthesized and spent catalysts were characterized by chemisorption, H2-TPR, TGA, XPS, SEM, XRD, BET, and Raman.

Acknowledgments
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Catalytic pyrolysis of MDF over beta zeolite-supported platinum

M. C. Rangel[1,2*], A. P. O. Oliveira[1], M. S. Carvalho[2,3], F. M. Mayer[1], C. F. Virgens[4]
[1]*Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil*
[2]*Universidade Federal da Bahia, Salvador, Brazil*
[3]*Universidade Estadual do Sudoeste da Bahia, Salvador, Brazil*
[4]*Universidade do Estado da Bahia, Salvador, Brazil*
[*]*maria.rangel@ufrgs.br*

Keywords: Beta zeolite, Platinum, Catalytic pyrolysis, Activation energy

Introduction. The growing demand for clean energy and environmental protection has pushed the government agencies to incentivate the development of new technologies for minimizing the impact of fossil sources. Among them, catalytic pyrolysis emerges as an efficient route for producing energy and chemicals from biomass, thanks to its flexibility, low cost, and simplicity. However, the process still needs active catalysts which can be tailored for each application. With this goal in mind, beta zeolites-supported platinum were evaluated in the catalytic pyrolisis of medium density fiber (MDF) residues, in this work. Thermokinetic parameters were also determined by Flynn-Wall-Ozawa (FWO), Kissinger-Ahakira-Sunose (KAS) and Friedman isoconversional methods.

Experimental/methodology. Samples of beta zeolite with different SAR (29, 42 and 75) were prepared as described elsewhere [1], but using silica extracted from coal ash from a thermoelectric power plant. Platinum (1%) was impregnated using hexachloroplatinic acid. The catalysts were characterized by Fourier transform infrared spectroscopy, X-ray diffraction (XRD), porosity measurements, nuclear magnetic ressonance, temperature programmed reduction (TPR) and acidity measurements by temperature programmed desorption of ammonia. MDF residues, previous treated [1] were mixed with the catalyst in the 1/0.2 (biomass/catalyst) ratio. Pyrolysis was performed on a TGA Q50 equipment (V6.7 Build 203, Universal) using around 7.0 mg of sample. The oven was heated from 25 °C to 900 °C at heating rates (β) of 5, 10, 15 and 20 °C min^{-1} under nitrogen flow (60 mL min^{-1}). The thermokinetic parameters were determined by Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Friedman methods.

Results and discussion. The XRD patterns of the catalysts showed typical profiles of beta zeolite, regardless platinum and the value of Si/Al ratio. As expected, the acidity decreased with increasing SAR for zeolites. Platinum decreased the amount and the strenght of acidic sites, the platinum-based sample with the lowest SAR (31) being the most acidic solid. Zeolites showed strong, moderate and weak acidic sites but for platinum-based samples only for the most acidic catalyst (SAR=31), weak sites were found. The TPR profiles were similar among the platinum-containing samples, indicating that the different values of SAR do not affect the interaction of platinum with beta zeolite. The curves show low and high temperature peaks, related to the reduction of platinum in weak and strong interaction with the support, respectively. Thermogravimetry results showed that platinum-based catalysts accelerate biomass decomposition mainly in the second stage, the main step of lignocellulosic biomass degradation, reaching the third stage at a lower temperature as compared to beta zeolites. Friedman method produced the highest correlation index (R^2=0.9757), indicating better adjustment to the pyrolysis data. The activation energy (E_a) average obtained by the Friedman method for the non-catalytic pyrolysis was 118.04 kJ mol^{-1}, which decreases over all catalysts (E_a=102.89 kJ mol^{-1}) indicating that the average activation energy for the decomposition of lignocellulosic componentes was decreased by beta zeolite. However, platinum increased the activation energy (E_a=112.95 kJ mol^{-1}). This finding can be associated with other reactions, catalyzed by platinum during MDF degradation. It was also noted that platinum increased the production of volatiles, during the second decomposition stage. Platinum can thus be useful to control the selectivity of beta zeolites, tailoring the catalysts for different applications.

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Perovskites-based catalysts for the production of renewable hydrogen

M. C. Rangel[1,2]*, G. A. dos Santos[2], Fernando A. Silva[3], F. M. Mayer[1], Nádia C. F. Machado[4]

[1]*Universidade Federal do Rio Grande do Sul, Brazil*
[2]*Universidade Federal da Bahia, Brazil*
*maria.rangel@ufrgs.br
[3]*Universidade Tecnológica Federal do Paraná, Brazil*
[4]*Universidade Estadual de Maringá, Maringá, Brazil*

Keywords: Perovskite, iridium, hydrogen, ethanol steam reforming

Introduction. Scientific, technological, and industrial development has enabled the gradual replacement of fossil fuels by renewable sources. Among them, bioethanol is a viable and promising alternative for producing hydrogen from steam reforming (ERS). However, its efficiency depends on the properties of the catalyst and then there is a constant investigation for active and selective catalysts which can also be resistant to coke formation. With this goal in mind, this work describes the synthesis and characterization of iridium supported on mixed oxides derived from nickel, cobalt, magnesium, and lanthanum perovskites for hydrogen production by ERS.

Experimental/methodology. Nickel and/or cobalt and/or magnesium and lanthanum perovskites ($La_{1-x}Mg_xNi_{1-y}Co_yO_3$; x = 0 and 0.5 and y = 0 and 0.5) were prepared by the decomposition of amorphous citrate method, followed by heating at 800 °C [1]. The perovskites were characterized and heated (10 °C min^{-1}) under gas flow (10% H_2/N_2) up to 700 °C, giving rise to nickel and/or cobalt supported on lantana with (or not) magnesium. The catalysts were passivated, impregnated with a solution of chloroiridic acid (1% w/w) and then heated (10 °C min^{-1}) under gas flow (10% H_2/N_2) up to 700 °C, giving rise to the iridium catalysts. The samples were passivated and named according to the metals: L (lanthanum), N (nickel), C (cobalt), M (magnesium) and I (iridium). They were characterized by thermogravimetry, Fourier transform infrared spectroscopy, X-ray diffraction, specific surface area (Sg) measurements, temperature programmed reduction and temperature programmed desorption of ammonia. The catalysts were evaluated in ESR at 1 atm and 500 °C, for 8 h. The reaction products (H_2, CO, CO_2, CH_4, ethane and ethene) were analysed by gas chromatography. After reaction, all catalysts were characterized by X-ray diffraction and Sg measurements .

Results and discussion. XRD patterns confirmed the formation of perovskites for all cases. Small amounts of other phases (NiO, La_2NiO_4, $CoMgO_2$, La_2NiO_4 and MgO) were also found depending on the composition of the catalyst. After reduction, all solids showed metal oxides, as well as metallic nickel and/or cobalt. Small amounts of other phases (NiO, CoO, $La_3Co_3O_8$ and $NiMgO_2$) were also detected indicating that nickel and/or cobalt were not completely reduced. The Sg ranged from 14 (LMNCI) to 26 $m^2\ g^{-1}$ (LMCI) for fresh catalysts and from 14 (LMNCI) to 39 $m^2\ g^{-1}$ (LMNI) for the spent ones. During ERS, the Sg increased for LMNI and LMCI while the others did not change. The main products of ERS were H_2 and CO_2, but other products (CO, CH_4 and C_2H_4) were also formed by parallel and consecutive reactions. All catalysts produced high amounts of H_2, a fact that was related to the high activity of the metals in ethanol dehydrogenation and in methane steam reforming (MSR). LMNCI catalyst produced the highest value, demonstrating the cooperative action among the metals. For the cobalt (LCI) and nickel (LNI) samples, magnesium decreased H_2 production and increased CH_4 and CO amount, indicating that MSR and the water gas shift reaction (WGSR) were inhibited by magnesium. A different behaviour was noted for the other samples, magnesium increasing H_2 and CO production while CH_4 amount was decreased. This means that the MSR was favoured by magnesium. Except for LCI, LMCI and LMNCI samples, the catalysts did not produce ethylene, the main coke precursor. Therefore, the catalysts are able to inhibit deactivation and increase their stability throughout the reaction. The LMNCI sample is the most promising catalyst producing the highest H_2 amount, the least amount of CH_4 and less than 1% of ethylene.

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Hydrothermal HDO of black liquor HTL oil and HTL oil model compounds

Sari Rautiainen[1*], Tyko Viertiö[1], Niko Vuorio[1], Kaarlo Huomo[1], Ludek Meca[2], Pavel Kukula[2], Juha Lehtonen[1]

[1] *VTT Technical Research Centre of Finland Ltd, Espoo, Finland*
[2] *Ranido s.r.o., Praha, Czech Republic*
[*] *sari.rautiainen@vtt.fi*

Keywords: Biofuel, black liquor, hydrodeoxygenation

Introduction. Black liquor (BL), a side stream from chemical pulping industry, is a promising feedstock for biofuels as it contains circa half of the energy of the lignocellulose. EU project Black Liquor to Fuel (BL2F) aims to develop a feasible route from black liquor to drop-in biofuels for aviation and shipping. In the first step, black liquor is treated under hydrothermal conditions to separate the cooking chemicals and produce hydrothermal liquefaction (HTL) oil from the organics [1]. The HTL oil is then further upgraded using catalytic hydrotreating using an integrated hydrothermal hydrodeoxygenation process. The aim of the hydrothermal hydrodeoxygenation (HDO) is to remove most of the oxygen and sulfur present in the feed and to stabilise the oil for easier transport and further upgrading at oil refineries. In this work, we study the hydrodeoxygenation of both model compounds and HTL oil in supercritical aqueous media.

Experimental/methodology. The HDO experiments were carried out in a batch reactor using sulfided NiMo catalysts and hydrogen gas. The catalyst supports were selected based on the stability tests in supercritical water conditions. Model compound studies were carried out using isoeugenol and 4-methylcatechol to represent the different functionalities present in the HTL oil. The products were analysed by GC-MS to assess the effect of the catalyst and reaction conditions on the product distribution. Similarly, experiments with HTL product were carried out in sub- and supercritical water conditions, and the effect on the degree of deoxygenation was studied.

Results and discussion. The HDO of the model compounds in aqueous media gave cresols as main products (Figure 1). The reaction conditions and catalyst had a clear effect on the conversion and the extent of cracking and hydrogenation of the aromatic ring. With the real HTL oil as a feedstock, the main parameter to be montored was degree of deoxygenation (DOD). The effect of the catalysts and reaction conditions on DOD will be presented.

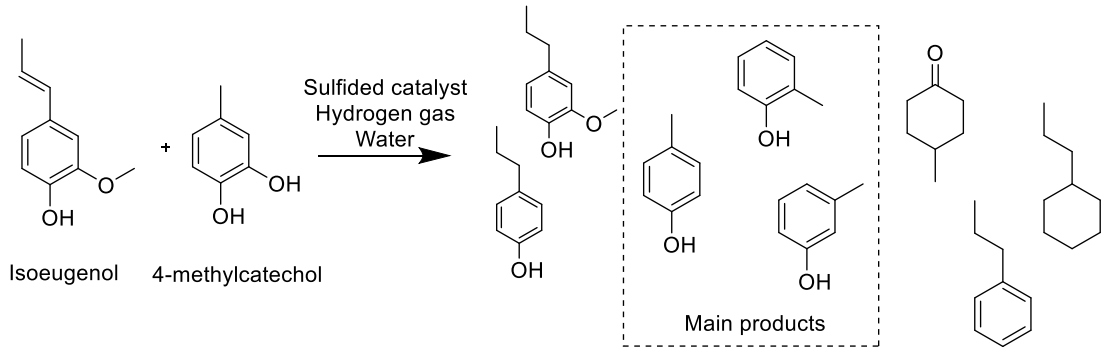

Figure 1. Hydrodeoxygenation of black liquor HTL oil model compounds in supercritical water.

Acknowledgments
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Catalytic hydrogenation/hydrogenolysis of glucose rich streams over biochar/activated carbon supported metal catalysts for the production of sorbitol and smaller diols/glycols

K. Rekos[1,2], A. Margellou[1,2], Ch. Wurzer[3], O. Mašek[3], A. Anukam[4], L. Matsakas[4], U. Rova[4], P. Christakopoulos[4], K. Triantafyllidis[1,2*]

[1]*Aristotle University of Thessalniki, Department of Chemistry, Thessaloniki, GR-54124, Greece*
[2]*Center for Interdisciplinary Research and Innovation (CIRI), Balkan Center, GR-57001 Thessaloniki, Greece*
[3]*UK Biochar Research Centre, School of GeoSciences, University of Edinburgh, EH93BF, Edinburgh, UK*
[4]*Biochemical Process Engineering, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, SE-971 87 Luleå, Sweden*
*ktrianta@chem.auth.gr

Keywords: hydrogenation/hydrogenolysis, sugar alcohols, diols, bio-based chemicals, biochar

Introduction

An important valorization route of biomass derived sugars, such as glucose and xylose, is their hydrogenation/hydrogenolysis to sugar alcohols (e.g. sorbitol, xylitol) and smaller diols/glycols (e.g. ethylene glycol, propylene glycol and glycerol), which can be utilized in the production of food ingredients, pharmaceuticals, polyesters, surfactants and functional fluids. Additionally, biomass can be converted to biochar via pyrolysis, which after appropriate physical/chemical activation can serve as micro/mesoporous metal support for the above said hydrogenation reactions [1-3].

Experimental/methodology

Model glucose aqueous solutions of relatively high concentration, ca. 5-20% were used as feedstock to study/optimize the reaction conditions (temperature, time, H_2 pressure) towards either increased sorbitol yield via hydrogenation or enhanced production of smaller diols/glycols via combined hydrogenation/hydrogenolysis. The metals tested as catalysts were Ru, Pt and Ni, each one exhibiting varying hydrogenation reactivity/selectivity towards the above targeted products. Commercial micro/mesoporous activated carbons as well as activated biochars, derived from miscanthus straw pyrolysis at 700°C, were used as metal supports. Optimization tests were conducted on small-size high pressure stirred batch reactors (50-100 mL). The hydrogenation of glucose was performed at 120-180°C, for 3-5h, at 30 bars H_2, while hydrogenolysis required more intense conditions, i.e. 200-220°C, 1-3h, 30-50 bars H_2. The optimized parameters and catalysts were then tested on a 5 Lit micro-pilot reactor working under batch/fed-batch and continuous flow conditions. The real biomass derived glucose feedstocks were obtained via a high-gravity enzymatic hydrolysis/saccharification of cellulose pulps obtained from organosolv fractionation of hardwood biomass. The products were analyzed by HPLC/RID, LC-MS, NMR, Karl-Fischer titrator, while the catalysts were characterized by XRD, BET, XPS, TEM.

Results and discussion

Glucose hydrogenation was optimized to over 90% sorbitol yield (at ~99% glucose conversion), mainly over Ru catalysts, with minor co-production of ethylene glycol (EG) and 1,2-propanediol (1,2-PDO). The biochar-based catalysts exhibited similar performance to that of the commercial activated carbons, via mainly affecting/promoting the dispersion of the active hydrogenation metal. Higher temperatures with noble metals, and mainly with Ni catalysts, favored the cascade hydrogenation-hydrogenolysis reaction pathways, leading to enhanced production of EG and 1,2-PDO, over sorbitol. The real cellulose hydrolysates feedstocks afforded similar reactivity and yields towards the targeted products, while upscale production was effectively verified in the micro-pilot reactor. Catalysts were also proven stable and reusable.

Acknowledgments

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Sorbitol aqueous phase transformation using cobalt aluminate- based catalysts under H_2 and N_2 atmosphere

A.J. Reynoso[1], J.L. Ayastuy[1], U. Iriarte-Velasco[2], L. Vivier[3], C. Especel[3], M.A. Gutiérrez-Ortiz[1].

[1]*Dept. of Chemical Engineering, Faculty of Science and Technology, UPV/EHU, 48940 Leioa, Spain.*
[2]*Dept. of Chemical Engineering, Faculty of Pharmacy, UPV/EHU, 01006 Vitoria, Spain.*
[3]*Université de Poitiers, CNRS UMR 7285 IC2MP, 4 rue Michel Brunet, 86073 Poitiers Cedex 9, France.*
[*] *joseluis.ayastuy@hu.eus*

Keywords: Biomass, Biofuels, Cobalt-based catalysts, Hydrogen.

Introduction. Sorbitol is a promising building block for the production of chemical that can be produced from renewable biomass, such as corn starch–based glucose and corn steep liquor. Transformation of sorbitol in aqueous phase can be tailored to selectively produce hydrogen (APR process) or heavier alkanes that can be used in the gasoline pool and other less oxygenated compounds (HDO) [1]. Hence, sorbitol is a pivotal platform molecule for the decarbonization of the economy.

$CoAl_2O_4$-derived catalysts and bimetallic Pt/$CoAl_2O_4$ have been successfully used for hydrogen production by glycerol APR [2]. In this work, a comparative approach for value-added chemical production from aqueous-phase sorbitol transformation under inert atmosphere and H_2 pressure has been carried out.

Experimental/methodology. Cobalt aluminate was synthesized by coprecipitation (xCoAl, x = 0.25-0.625 Co/Al molar ratio) and Pt-modified catalyst (Pt = 0.3 and 1.0 wt.%) was prepared by wet impregnation (xPt/CoAl). The physico-chemical properties of the freshly reduced and spent catalysts were evaluated by a sort of techniques. A 300-mL stainless steel batch reactor (Autoclave Engineers) fitted with systems for liquid and gas sampling was used for the catalytic transformation of 6.25 wt.% sorbitol aqueous solution. The tests were carried out at 240 °C/60 bar, under H_2 and N_2 atmosphere, for 8 h.

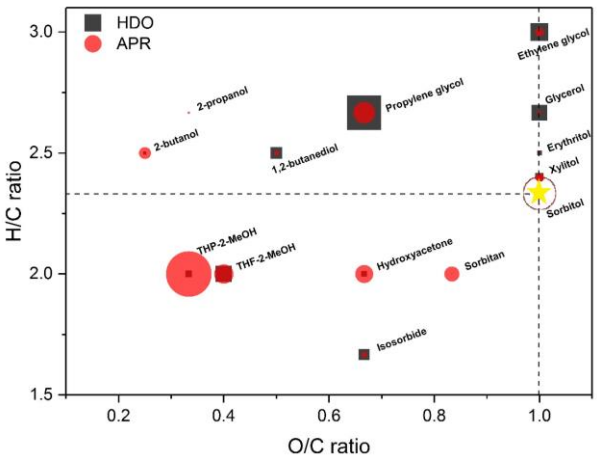

Figure 10. Van Krevelen representation (H/C vs. O/C atomic ratio) of liquid products obtained during sorbitol transformation (HDO vs APR) over 0.3Pt/CoAl.

Results and discussion. All the catalysts were very active for the transformation of sorbitol under H_2 pressure (HDO), achieving complete conversion after 6 h reaction. Pt containing bimetallic catalysts were the most active among all. Propylene glycol and ethylene glycol were the main liquid products obtained for all catalysts. In short, due to the predominance of surface basic sites, our Co-containing catalysts promoted the retro-aldol condensation route for sorbitol HDO. Under N_2 atmosphere (APR), on contrary, none of the studied catalyst reached the complete sorbitol conversion in 8 h of reaction (maximum conversion of 93.5% for 1Pt/CoAl and 92.6% for 0.3Pt/CoAl). In sorbitol APR, the most relevant products were tetrahydropyran-2-methanol (THP-2-MeOH) and hydroxyacetone. Sorbitol HDO over 0.3Pt/CoAl catalyst yielded more hydrogenated liquids (higher H/C ratio) than sorbitol APR, which resulted in a higher yield towards liquids with low H/C and O/C ratio (Fig. 1).

Acknowledgments

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Conversion of glucose to formic acid on VO/CNTs funtionalized catalysts

P. Rodríguez[1,2*], D. Paz[1,2], C. Parra[1,2,3], G Pecchi[1,2], C. Sepúlveda[1,2]

[1]*Depto Físico-Química, Fac Cs Químicas, Universidad de Concepción, Chile*
[2] *Millennium Nuclei on Catalytic Process towards Sustainable Chemistry (CSC), Chile*
[3] *Centro de Biotecnología, Universidad de Concepción, Chile*
[*]*pedrrodriguez@udec.cl*

Keywords: formic acid, funtionalized CNTs, glucose, vanadyl

Introduction. Starch is a lignocellulosic derivatives that can be valorized in an aqueous medium using heterogeneous catalysts to added-value chemicals such as formic acid (AF), which is an H_2 storage molecule [**1**]. As catalytic systems, one of the advantages of carbon nanotubes (CNT) as supports is the possibility of modifying their acid-base properties through a surface functionalization (CNT-f) [**2**], and in the active phase, the vanadyl cation (VO^{2+}) exhibits redox characteristics [**3**], which are essential for the starch conversion reaction. In this work, the catalytic conversion of glucose to formic acid in aqueous medium was used as a representative starch molecule on VO (10 wt%) supported on CNT and CNT-f (f= COOH and NH_2) catalysts denoted as VO/CNT, VO/CNTCOOH and VO/CNTNH_2

Experimental/methodology. The catalysts were syntetized by wetness impregnation of 10 wt% of VO on the CNT and CNT-f supports. The materials were characterized by X-Ray diffraction (XRD), physisorption of N_2 (BET)at 77 K and XPS measurements. The conversion of glucose (15 g*L^{-1}) was carried out in a batch reactor at 700 RPM, 30 bar of O_2, 140 °C and 50 mg of catalysts in aqueous medium.

Results and discussion. XRD of the VO-impregnated CNTs are very similar to the CNTs used as supports; the BET area of the supports decreases 38% due to the incorporation of VO. XPS analysis suggests that the CNTs are functionalized at a lower percentage than nominal. The VO leaches from the CNTs and CNT-f, in the first reation cycle. The solids are active in the catalytic conversion of glucose to FA, all exceeding 85% conversion of glucose at 140 °C and 180 min of reaction. At 20% isoconversion the selectivity to FA has the following order VO/CNT>VO/CNTCOOH>VO/CNTNH_2 with 57%, 54% and 45% respectively. The presence of vanadium leads to the catalysts being efficient in the production of formic acid as the major product.

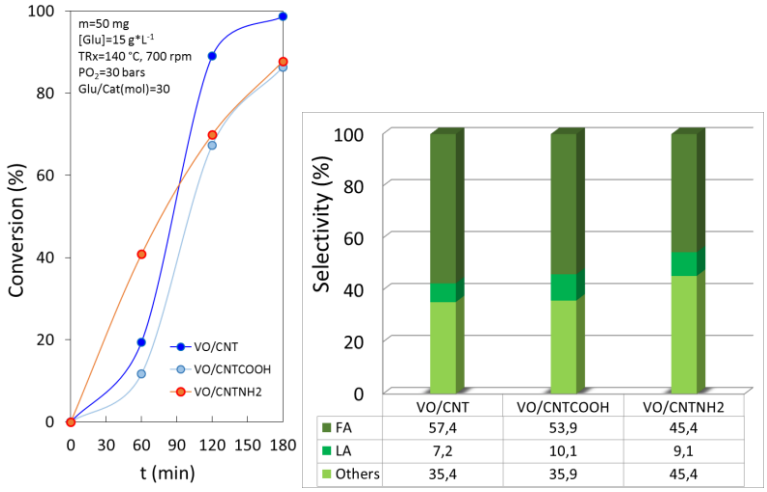

Figure 1. Glucose conversion curves and selectivity to FA on VO/CNT-f catalysts.

Acknowledgments
The authors thank ANID Fondecyt 1210142 and 1220130, ANID Millennium Science Initiative grant NCN2021-090 for the financial support.

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H_2 generation by the photoreforming of biomass-derivatives using TiO_2 modified with C and Cu

S. Belda-Marco, M. Bouchabou, M.A. Lillo-Ródenas, M.C. Román-Martínez*

MCMA research group, Department of Inorganic Chemistry and Materials Institute (IUMA). Faculty of Sciences. University of Alicante, Alicante, Spain
* *mcroman@ua.es*

Keywords: Cellulose, Photoreforming, TiO_2, Carbon, Copper, Hydrogen.

Introduction.

The growing concentration of CO_2 in the atmosphere, mainly due to the high energy demand and the current model based on fossil fuels, is becoming a serious problem. Among the several approaches to address this problem, finding a suitable way to produce green hydrogen as an alternative fuel is a central one, for which the use renewable resources is mandatory. In this context, the present work deals with the photoreforming of biomass or biomass components or derivatives, like cellulose, using TiO_2-based photocatalysts [1]. In order to improve the efficiency of bare titania, photocatalyts have been prepared by means of doping it with carbon and/or by the incorporation of metal species.

Experimental/methodology.

A series of carbon-doped titania photocatalysts were prepared by hydrothermal synthesis of TiO_2 (12 h, 180 °C) using titanium tetraisopropoxide, and adding either sucrose [2] or graphene oxide as dopant sources. Bare TiO_2 was prepared, as well, by the same method and conditions. Copper was added to the composition of the resulting TiO_2 and TiO_2-C samples by impregnation with an aqueous solution of copper nitrate [3]. The following characterization tecniques were used: ICP-OES, XRD, XPS, and TEM. The photocatalytic activity tests were performed in a Heraeus UV-RS-2 glass reactor with a 150 W mercury lamp (365 nm), using 1 g cellulose, 20 mg photocatalyst and 500 mL distilled water. The generated gas was swept by He flow (60 mL/min) and continuously analysed by mass spectrometry. The resulting solution was analysed by ionic chromatography and by the determination of total organic carbon (TOC).

Results and discussion.

XRD data show that anatase is the crystalline phase of the synthesize photocatalysts. XPS results reveal that copper is mainly present as Cu(I) and/or Cu(0). The tested photocatalysts show, in general, a high hydrogen production (1500-1900 $\mu mol \cdot h^{-1} \cdot g \cdot cat^{-1}$), being the catalyst that contains carbon from succrose and copper the most active. The activity of these catalysts is noticeably higher than the previously determined for the commercial titania P25 (hydrogen production = 595 $\mu mol \cdot h^{-1} \cdot g \cdot cat^{-1}$) [3]. The obtained results show an important effect of both, carbon doping and metal incorporation, in the photocatalytic performance of TiO_2.

Acknowledgments
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Sn_xNi_y alloys supported on Ce-Zr mixed oxides for the aqueous phase reforming reaction of ethylene glycol: influence of the pH and the active metal phase on the reaction outcome

C.Rosmini[1*], M. Pazos Urrea[2], E. Tusini[3], S. Indris[4], A. Zimina[5], J.-D. Grunwaldt[3,5], M. Rønning[2], M. Dimitrov[1].

[1]Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria. [2] Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway. [3]Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany. [4]Institute for Applied Materials, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany. [5]Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany.

**consolato.rosmini@orgchm.bas.bg*

Introduction

In recent years, aqueous phase reforming (APR) of polyols and sugars is envisaged as a possible replacement of the current hydrogen production methods such as steam reforming and auto thermal reforming, given its low operating temperature, moderate pressures and not least, the ecological advantage of converting and utilizing biomass instead of fossil fuels [1]. Nickel catalysts in this reaction are known to have very good biomass conversions but also a strong selectivity for methane at the expense of the hydrogen final yield. Shabaker et al. [2] demonstrated how the addition of tin to Ni-Raney catalysts (Ni concentration >60%wt.) decreased the selectivity to the methanation reaction. In this study, we aim to substantially decrease the nickel concentration in the catalyst and by varying the reaction parameters, to preserve more than encouraging results on the APR process under batch conditions.

Experimental/methodology

Different compositions of $Sn_xNi_y/Ce(Zr)O_2$ were prepared by micellar-assisted synthesis and following reduction and sintering process. The catalysts were characterized by X-ray Powder Diffraction, ^{119}Sn-Moessbauer spectroscopy, High Resolution-Trasmission Electron Microscopy, H_2-Temperature Programmed Reduction, H_2-Chemisorption and *ex-situ* X-ray Adsorption Spectroscopy. The APR reaction was carried out in a batch "Parr" reactor, processing an aqueous solution of ethylene glycol 6 % wt. at a screening temperature of 270 °C, an initial pressure of 20 bar and changing the initial pH.

Results and discussion

The combination of the information obtained from the X-Ray Powder diffraction and High Resolution-Trasmission Electron Microscopy analysis of the mixed metal oxides shows a fine dispersion and co-existence of the tin and nickel oxides within the $Ce(Zr)O_2$ catalytic support. The reduction process leads to the formation of two different combinations of Sn_xNi_y alloys clearly differentiated and quantified by ^{119}Sn-Moessbauer spectroscopy. The two different combinations of active metallic alloys make significant differences both in terms of conversion and hydrogen yield and in terms of selectivity in the methanation reaction in comparison with the monometallic nickel catalyst. It is also shown how a change in operating conditions, such as a change in the initial pH, influences the development of the reaction decisively.

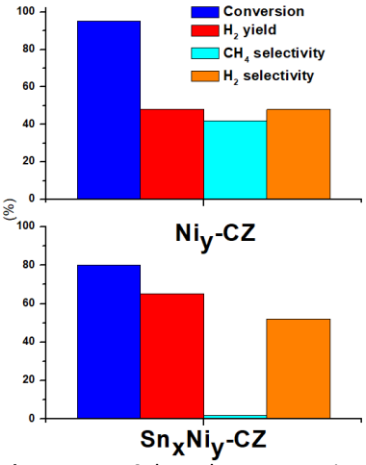

Figure 1: Selected comparative collection of conversion values, selectivity and hydrogen yield of a bimetallic Sn_xNi_y catalyst and its monometallic counterpart (Ni_y).

Acknowledgments

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Controlled size and location of Ru nanoparticles in titania supported catalysts for selective synthesis of platform molecules from biomass

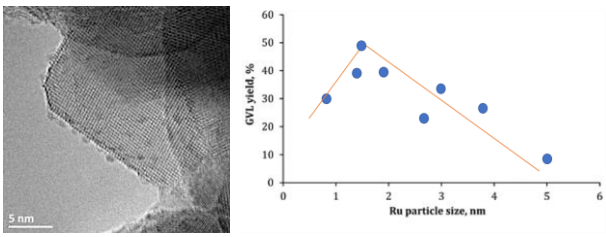
Agnieszka Ruppert[1*], Marcin Jędrzejczyk,[1] Nicolas Keller[2]

[1] *Institute of General and Ecological Chemistry Faculty of Chemistry Łódź University of Technology ul. Żeromskiego 116 90-924 Łódź (Poland)*
[2] *Institut de Chimie et Procedes pour l'Energie l'Environnement et la Sante (ICPEES) CNRS, University of Strasbourg 25 rue Becquerel 67087, Strasbourg (France)*
[*] *Corresponding Author's E-mail address: agnieszka.ruppert@p.lodz.pl*

Introduction. Biomass is considered a highly relevant sustainable source of energy and organic carbon for today's technological society, so that it is pivotal to industrial renewal for covering the future needs of chemicals, energy and fuels. Highly valuable chemicals that can be obtained from biomass are called platform molecules. Typically, they would find application in more than one industrial sector, and they would be crucial in future biorefinery schemes. Among them, 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) show a great potential as they can be converted to newly recognized attractive chemicals, including 2,5-bishydroxymethylfuran (BHMF), gamma-valerolactone (GVL), dimethylfurfural (DMF) to name a few. The main challenge associated with the use of these intermediates is their rich chemistry and, hence, difficulties in getting high selectivity to the final targeted products. Therefore, we designed the methodology allowing the synthesis of metal nanoparticles of controlled size and location using a versatile photon-assisted method allowing for the tuning of the particle size to optimal value [1]

Methodology. The strategy of solar photon-driven assisted synthesis method uses the redox photoactivity developed by the surface of the host semi-conductor used as support when activated upon suited irradiation. It relies on the promotion of electrons from the valence to the conduction band of the semi-conductor, further able to reduce pre-adsorbed metal ions at the semi-conductor support surface [1]. 1%Ru/TiO_2 catalysts prepared according to this methodology were compared to their counterparts prepared by a span of standard methods. Their catalytic efficiency was tested in several reactions like: (1) hydrogenation of LA with formic acid as hydrogen source to GVL (biofuel additive) and (2) HMF hydrodeoxygenation towards DMF (biofuel additive) or BHMTHF (bio-plastic precursor).

Results and discussion. This versatile methodology allows for the synthesis of well-defined metal nano-particles on the support and additionally permits a fine control over both the size and the narrow distribution of the supported nanoparticles. Thanks to the control of synthesis parameters like irradiation time or photonic flux, we were able to elaborate catalysts with average Ru size of in the range 0.6- 4.9 nm. We demonstrated that the size of the Ru nanoparticles is one of the key parameter strongly influencing both activity and selectivity in the studied reactions. For example, an optimum nanoparticle size of 1.5 nm was observed for 1%Ru/TiO_2 in the case of LA hydrogenation with FA used as hydrogen source. Smallest Ru particles (0.6 nm) were very susceptible to sintering and carbon deposit formation, whereas too large particles influence the adsorption strength and did not provide enough active sites. Besides the dominant effect of the particle size, other parameters like metal-support interaction, Ru oxidation state, catalyst acidity and presence of residual chlorine from the $RuCl_3$ precursor in the upper monolayer were also thrully discussed.



a) HRTEM of a 1% Ru/TiO_2 catalyst with a Ru nanoparticle size centered on 0.6 nm. b) Influence of the Ru nanoparticle size on GVL yield [1]

Acknowledgments

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Continuous hydrocyclization of aqueous levulinic acid to *γ*-valerolactone over bifunctional Ru/$NbOPO_4$/SBA-15 catalyst under mild conditions

Mariappan Mani[†¥], Mariyamuthu Mariyaselvakumar[†], Ajaikumar Samikannu[ŧ], Asit Baran Panda[¥‡], Lakhya Jyoti Konwar[†¥], Jyri-Pekka Mikkola[ŧ‡]

† Inorganic Materials and Catalysis Division, CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar, 364002 Gujarat, India

[¥]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India

‡ CSIR—National Metallurgical Laboratory, Jamshedpur 831007, India

ŧTechnical Chemistry, Department of Chemistry, Chemical-Biological Centre, Umeå University, SE-901 87 Umeå, Sweden

‡Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Åbo-Turku, FI-20500, Finland

Introduction

Levulinic acid (LA) is a well-known product of hexose sugar hydrolysis/dehydration and is inexpensively obtained by the decomposition of cellulosic feedstocks. Levulinic acid is an attractive platform material for the production of s range of chemical products, including methyltetrahydrofuran, γ-valerolactone, 1,4-propanediol, angelicalacotone, diphenolic acid and levuilinate esters (Fig. 1.). Among the various levulinic acid derivatives, γ-valerolactone (GVL), in particular, is of significant commercial importance, owing to its usefulness as a solvent, food additive, fuel component, and as a precursor for high-value chemicals (linear α-olefins, esters) and fuel range synthetic hydrocarbons. Although easily produced by hydrogenation of LA over Ru, the commercial usefulness of Ru-based catalysts for GVL production has been limited by deactivation issues resulting from (a) the leaching of Ru species through the formation of Ru–carboxylate complexes with levulinic acid (pKa ~4.59) in liquid phase (especially in water), (b) deposition of carbonaceous impurities (particularly in non-aqueous solvents) and (c) sintering and coking of Ru-nanoparticles in vapor phase reactions. The aim of the present work was to develop an active, selective, and stable catalyst for continuous hydrocyclization of aqueous LA to GVL under low-temperature conditions (≤100 °C).

Experimental

Aqueous phase hydrogenation of levulinic acid was performed under batch as well as, continuous flow conditions at 10 bar H_2 pressure using custom-made lab-scale reactors. In all experiments free flowing catalyst particles sized between 50–150 µm were used. All hydrogenation catalysts were obtained by the incipient wetness impregnation method using $RuCl_3.xH_2O$ as a Ru source.

Results and discussion

Herein, for the first time we demonstrate that surface acid-base properties of support have a marked effect upon the performance and stability of supported Ru catalysts upon hydrocyclization of aqueous LA to GVL in liquid phase. Among the tested catalysts, a bi-functional Ru/$NbOPO_4$/SBA-15 catalyst incorporating highly dispersed redox Ru sites and well balanced strong Brønsted acidic sites (optimum B/L and M+S/W ratio) outperformed the benchmark monofuncational (Ru/SBA-15, Ru/MCM-41) and physically blended bi-functional catalysts (Ru catalysts mixed with acid co-catalysts e.g. $NbOPO_4$/Amberlyst-15). Further, the catalyst also demonstrated remarkable stability in a fixed-bed reactor, maintaining high activity and GVL selectivity (72-86%) during ca. 300 h time on stream operating at 10 bar, 90-100 °C under varying H_2/levulinic acid flow rates, corroborating its potential for large scale GVL production under continuous flow conditions. The exceptional performance and durability of the bi-functional catalyst was attributed to the presence of well dispersed hydrothermally and chemically stable acid ($NbOPO_4$) and redox (Ru) sites.

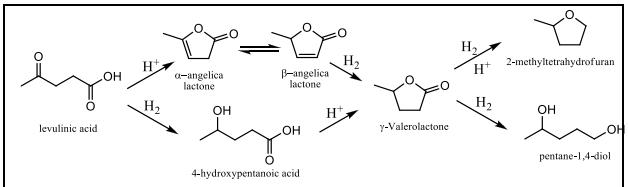

Fig. 1. Reaction network for the hydrogenation of levulinic acid

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On the promoting effects of cobalt and nitrogen over copper-based catalysts to produce hydrogen *via* methanol steam reforming

J.L. Santos[1,*] and J. Gascon[1].

[1]*1KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST)*
[*]*jose.santos@kaust.edu.sa*

Keywords: H_2 production, MeOH steam reforming, copper-doped catalysts, bimetallic catalysts.

Introduction.

In the future energy transition away from fossil fuels for mobile applications, hydrogen appears to become a crucial energy carrier. Methanol Steam Reforming (MSR) is suggested as a possible alternative source to produce hydrogen, primarily because of its high yield and convenience. Although since 1985, $Cu/ZnO/Al_2O_3$ with a copper content of 35–50 wt.% has been the most used catalyst, several noble and non-noble metals, as well as groups 8-10 metals-based catalysts, have already been examined [1]. However, there is still a lack of knowledge about the catalytic performance of bimetallic systems. The promoter roles of cobalt and nitrogen in copper-based catalysts with low copper loading have thus been studied in this work.

Experimental.

A series of copper-zinc-based catalysts, supported on alumina and doped with cobalt and nitrogen, have been synthesized by coprecipitation. The co-precipitation of the nitrate salts was conducted for 48 hours at room temperature, with magnetic stirring, at a constant pH of 10 (enabled by Na_2CO_3 and NaOH). The solid was recovered by filtration after stirring, dried at 100°C overnight, and then calcined at 350°C for five hours. In a high throughput reactor system with four parallel stainless-steel reactors, feeding a 1/1 water/methanol combination, powdered and unreduced catalysts were tested from 150 to 350 °C. Additionally, a series of tests consisting of five successive cooling-heating cycles and a continuous cycle for more than 50 hours were used to assess the stability of the synthesized catalysts.

Results and discussion.

On a copper-zinc catalyst supported on alumina, the promoter effects of cobalt and nitrogen have been studied. The average particle size of metallic copper decreased with the addition of cobalt and nitrogen. At the same time, cobalt enhanced copper's reducibility, lowering its reduction temperature by more than 20°C. Nitrogen addition resulted in an increased aluminum loading, which reduced the quantity of copper leached through the formation of tetraamine copper (II) and did not change the copper's reducibility.

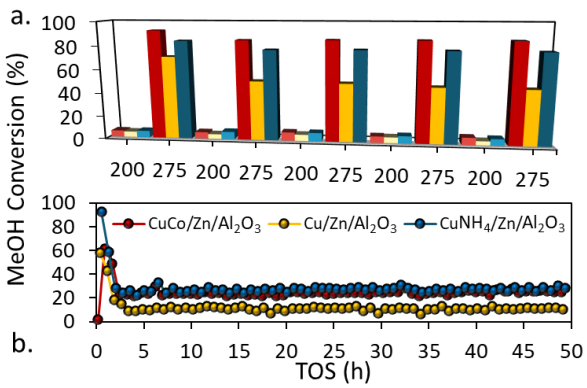

Figure 1a. *Heating-cooling cycles test at 200 and 275°C and* ***b.*** *50 h. stability test.*

Although the catalytic performance of the copper-zinc catalyst was improved by both cobalt and nitrogen doping, the Co-promoted the Reverse Water Gas Shift (RWGS), lowering the hydrogen yield. Nitrogen doping, however, only enhanced the MSR reaction. The stability of the promoted copper catalysts remained unchanged over the time on stream, even after five cooling-heating cycles and more than 50 hours of reaction at 230°C.

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Hydrodeoxygenation of BSFL lipids

Jon Selimi[1*], Christian Hulteberg[1], Jens Melder[2]

[1]*Department of Chemical engineering, Lund University, Lund, Sweden*
[2]*Institute for Fuel Chemistry, DLR, Stuttgart, Germany*
[*]*jon.selimi@chemeng.lth.se*

Keywords: HDO, hydrodeoxygenation, lipids, fuel upgrading, biofuel

Introduction. There is a growing need for alternatives to fossil fuels for shipping and aviation [1]. In this research, we worked with lipids from black soldier fly larvae (BSFL) fed with sugars derived from municipal solid waste. Upgrading the fatty substance through hydrodeoxygenation could show to be a promising path for the generation of fuels coming from second-generation feedstocks. Research has been done on HDO of oils with a high oxygen content[2,3], although there is lacking research on BSFL lipid.

Experimental/methodology. The experiments were performed in a 500 mL size batch autoclave reactor at temperatures ranging from 250°C to 450°C and with initial hydrogen pressures between 30 barg and 70 barg. Lipid oil in wax form was supplied by Enorm Biofactory in Denmark while the NiMo/alumina catalyst used in the hydrodeoxygenation tests was synthesized using commercially available precursors.

Results and discussion. Oil samples were analyzed by elemental analysis for oxygen content. As expected, temperature and pressure had a significant impact on hydrodeoxygenation. An optimal temperature for lower pressures (30 bar abs initial pressure) was found to be at around 375 °C. At lower temperatures, higher oxygen removal was achieved with higher hydrogen pressure. Further work will be done to optimize these parameters.

Table 1. Table of

Sample	Temperature (°C)	Pressure (bar abs)	Oxygen %
A	350	30	1,991
B	350	70	0,293
C	450	30	0,418
D	375	30	0,525
E	300	30	8,296
F	250	30	11,687
G	300	70	3,821
H	250	70	12,213
Raw	-	-	12,860

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Oxidation of furfural to maleic acid on $LaCo_xFe_{1-x}O_3$@C catalysts

D. Díaz[1], C. Herrera[1,2], G. Pecchi[1,2], C. Sepúlveda[1,2*]

[1]*Depto Físico-Química, Fac Cs Químicas, Universidad de Concepción, Chile*
[2] *Millennium Nuclei on Catalytic Process towards Sustainable Chemistry (CSC), Chile*
[*]*cathsepulveda@udec.cl*

Keywords: furfural, oxidation, Co effect.

Introduction. Green Chemistry is oriented towards the design of chemical processes of renewable raw materials that reduces or eliminates the generation of waste and that allow obtaining products with high added value. Biomass is a renewable source that can be used for a large number of applications, where furfural is a promising platform intermediate molecule from hemicellulose transformation with several green applications, and its low oxygen content makes it a promising raw material in the fine chemical industry[1]. Maleic acid (MA) is one of the top 12 biobased molecules of the Department of Energy of US, and it can be obtained from furfural oxidation through 2(5H)furanone and 2-hydroxyfuran as intermediates[2, 3]. In this work the catalytic evaluation of $LaFeO_3$@C, $LaCoO_3$@C and $LaCo_xFe_{1-x}O_3$@C (x=0.0, 0.1, 0.3. 0.5, 0.7, 0.9, 1.0) perovskites in the oxidation of furfural is reported.

Experimental/methodology. The pure and substituted perovskites were synthesized using the citrate method and characterized by N_2 physisorption at 77 K, thermal programmed reduction (H_2-TPR), X-Ray diffraction (XRD) and thermal programmed desorption of CO_2 (CO_2-TPD). The catalytic activity was evaluated in a semi-batch reactor in the oxidation of furfural at 150 °C, 30 bar of pure O_2 and 50 mg of perovskites as catalysts.

Results and discussion.

The Figure 1 shows the selectivity calculated at 25% of furfural conversion over the perovskite@C catalysts, where almost 100% of MA selectivity on $LaFeO_3$@C catalyst is obtained. After Co addition, a drastically decrease of MA selectivity to around 60 % and 40% of 2-hydroxyfuran is detected over all Co-substituted and pure $LaCoO_3$@C. These results suggests that the presence of Co species change the oxidative properties of the $LaFeO_3$@C catalysts by formation of more stable intermediates on the catalytic surface such 2-hydroxyfuran. The physicochemical characterization results of the Co-substituted perovskite@C catalysts shows a modification of reduction temperatures of Co and Fe oxides, several changes in the intensity and temperature of CO_2 desorption signals and an important decrease of the specific surface area in comparison to pure $LaFeO_3$@C and $LaCoO_3$@C catalysts. These results suggest that Co addition promotes an interaction between Co and Fe oxides modifyng the electronic and basic properties which change the surface catalytic behavior.

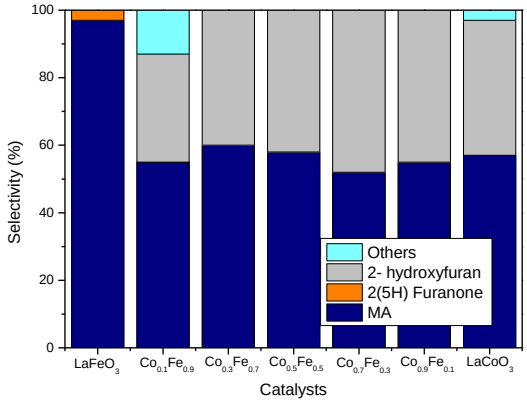

Figure 1: Selectivity at 25 % of furfural conversion.

Acknowledgments

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Protection strategy for selective oxidative esterification of HMF-dimethylacetal to dimethylfuran-2,5-dicarboxylate

*N. Sheet, N. Arai, J. J. Wiesfeld, R. Osuga, A. Fukuoka, K. Nakajima**
Institute for Catalysis, Hokkaido University, Sapporo, Japan
nakajima@cat.hokudai.ac.jp

Keywords. Protection strategy, biomass conversion, oxidative esterification, dimethylacetal functionality.

Introduction. 5-Hydroxymethylfurfural (HMF), a biomass-derived furan compound, is one of the versatile platform chemicals to produce various value-added building blocks of advanced biobased polymers.[1] However, chemical reactions of HMF accompanies severe and complex side reactions predominantly in concentrated solutions and produces insoluble polymerized species, so-called humins. Protection of the reactive formyl group with 1,3-propanediol (PDO) to form a six-membered acetal ring enabled the use of concentrated solutions (10-20 wt%) in various redox reactions and ensured high productivity of the intended products.[2-4] Herein, we applied dimethylacetal-protected HMF (HMF-acetal) in the oxidative esterification with supported Au catalysts for the stepwise synthesis of dimethylfuran-2,5-dicarboxylate (MFDC).

Methodology. HMF-acetal was prepared by the acetalization of HMF with methanol and supported gold catalysts were synthesized by the deposition-precipitation method.[3] Oxidative esterification reactions of HMF, HMF-acetal and MFFC-acetal (the dimethylacetal form of methyl 5-formyl-2-furancarboxylate) in methanol were conducted in pressure-resistant Teflon-lined stainless steel autoclave reactors. The mixture of a methanolic substrate solution (100 mg, 10-20 wt%), Au/CeO_2 (100 mg) and Na_2CO_3 (1 mol%) was stirred at 373 K for 2 h under pressurized oxygen (0.9 MPa). After reactions, the reaction mixtures were diluted with ethyl acetate (50 mL) to dissolve all products and analyzed with Gas Chromatography (Shimadzu, GC-2014).

Results and Discussion. Oxidative esterification of HMF-acetal at 10-20 wt% afforded MFFC-acetal exclusively in high yields (>90%). In contrast, the reactions of non-protected HMF under the same reaction conditions gave the mixtures of 5-hydroxymethylfuran-2-methyl carboxylate (MHFMC), MFDC and humin-type byproducts (Figure 1). Kinetics studies revealed that protecting highly reactive formyl group of HMF with dimethylacetal functionality not only suppresses byproducts formation but also facilitates the rate of first reaction step to convert -CH_2OH in HMF-acetal to -$COOCH_3$ (Figure 2). The dimethyl-acetal group did not undergo oxidative esterification under such mild reaction conditions, while increase in reaction temperature resulted in severe byproduct formation, which prevents the direct synthesis of MFDC from HMF-acetal.

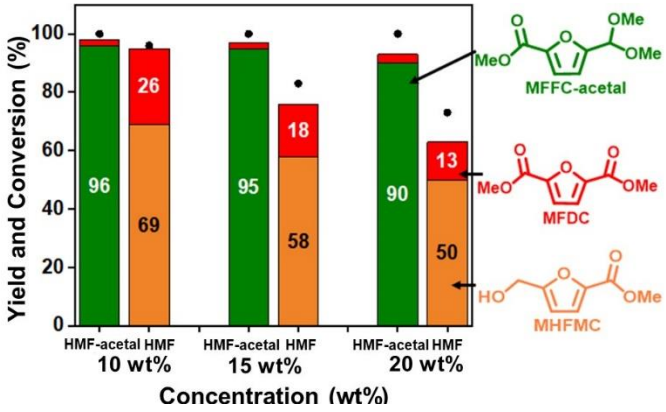

Figure 1. Oxidative esterification of HMF-acetal vs HMF.

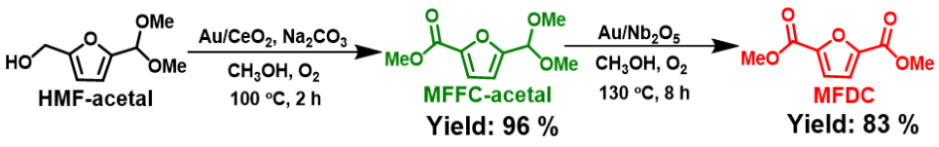

Figure 2. A stepwise route to synthesize MFDC from HMF-acetal with two supported Au catalysts.

Therefore, a two-step process was designed to synthesize MFDC selectively from concentrated methanolic solutions of HMF-acetal. The second step, oxidative esterification of MFFC-acetal to MFDC, was conducted with crude MFFC-acetal and Au/Nb_2O_5, which produces MFDC in an 83% yield (A 10 wt% MFFC-acetal solution, Au/Nb_2O_5, 130 °C, 0.9 MPa O_2, 8 h) (Figure 2). Thus, the present approach opens a new stepwise route for MFDC production with an HMF-acetal and two supported Au catalysts.

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Interfacial oxygen vacancy over Ni/CeZrOx catalysts for ethanol steam reforming: Ni-support interaction and resistance to coking

Mingyan Wang, Azam Jamsaz, Ngoc Nhiem Pham, Thi Van Anh Hoang, Eun Woo Shin*
School of Chemical Engineering, Univerisity of Ulsan, Ulsan, Republic of Korea
**Corresponding Author's E-mail address: ewshin@ulsan.ac.kr*

Introduction. Recently, ethanol steam reforming (ESR) has received great attention as an environmentally friendly and clean H_2 production process. Ethanol's advantages include its non-toxicity and ease of handling and transport. Moreover, when bioethanol produced mainly through fermentation of saccharide is used as a feed, carbon neutrality can also be achieved because CO_2 generated from reforming can be reabsorbed into biomass as a raw material [1-2]. Ni-based catalysts lead to a high hydrogen yield at high reaction temperatures due to their ability to cleave C–C and C–H bonds. It is well known that $Ce_xZr_{1-x}O_2$ supports have a high OSC with oxygen vacancies, which plays an important role in enhancing catalytic activity under reducing and oxidizing conditions [3]. Therefore, tracking the reaction pathway over oxygen vacancies is essential for not only elucidating the ESR mechanism but also finding a key property to improve the catalytic performance. In this study, two types of Ni/$CeZrO_X$ catalysts were separately synthesized with different Ni contents. The Ni/$CeZrO_X$ catalysts were prepared by impregnating Ni species into the $CeZrO_X$ support or by one pot (OM) method to investigate not only the formation of oxygen vacancies by Ni–support interaction but also the role of those vacancies in the coking behavior of ESR.

Experimental/methodology. The ethanol steam reforming tests were performed at atmospheric pressure in a fixed-bed vertical quartz tube reactor (450 mm in length and 10 mm in inner diameter). In all tests, 0.3 g of catalyst was placed on a frit inside the reactor with glass wool. The catalyst was reduced in situ in flowing H_2 (6 mL/min) with He (30 mL/min) at 750 °C for 2 h. The reaction tests were conducted for 8 h at 550 °C. The steam-to-carbon mole ratio (S/C) was fixed at S/C = 3 for every reaction test. The Ni/CeZrOx catalysts were characterized by various tools including N_2 adsorption-desorption technique, H_2-TPR, Raman spectroscopy, XRD, TEM, and XPS.

Results and discussion. From diverse characterization results, it was confirmed that the Ni/CZ-OM catalysts had highly dispersed Ni nanoparticle and well devoloped oxygen vacancy in the interfacial region,which was caused by the Ni-support interaction during the preparation process. Figure 1 shows the coke amounts generated during the reaction tests. A lot of coke were generated over the Ni/CZ catalysts while coking barely occurred over the Ni/CZ-OM catalysts. The high Ni dispersion and neighboring oxygen vacancy over the Ni/CZ-OM catalysts suppressed coking behavior during the ESR.

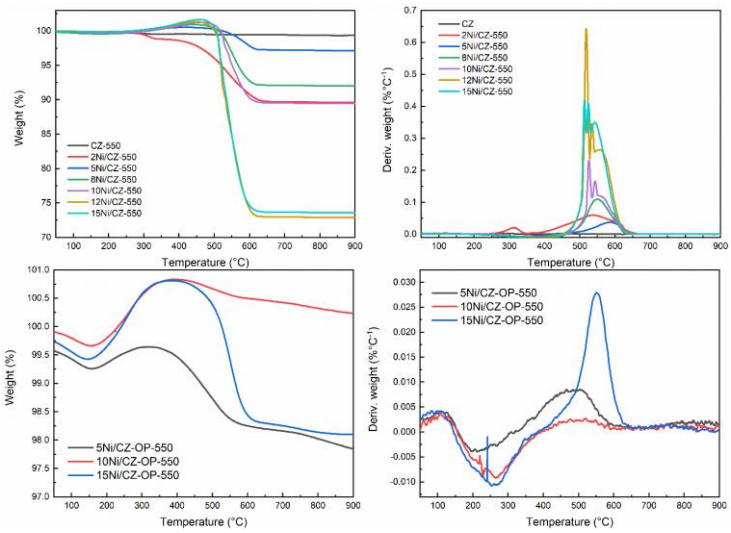

Figure 1. TGA and DTGA results of the spent Ni/CZ catalysts.

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Hydrogenolysis of xylitol to glycols and mono-alcohols over nickel supported on sulfated-zirconia

Talent Ngwenya[1], Alisa Govender[2], Jaco Olivier[3] and Mzamo Shozi[1*]

[1]*School of Chemistry and Physics, University of KwaZulu-Natal, Durban, 4000, South Africa*
[2]*Group Technology, Sasol South Africa, Sasolburg, 1974, South Africa*
[3]*Nelson Mandela University, Summerstrand, Port Elizabeth, 6001, South Africa*
[*]*shozim2@ukzn.ac.za*

Keywords: nickel, sulfated-zirconia, xylitol, glycols, mono-alcohols

Introduction. Replacing fossil-based feedstocks with biomass-derived resources to produce renewable fuels and chemicals addresses chemical industries' challenges.[1] In this context, xylitol is one key intermediate platform to explore. It can be hydrogenated into a variety of important chemicals, such as ethylene and propylene glycol which are used as monomers in the synthesis of polyester fibers, antifreeze and coolants and butanediols used for manufacturing plastics and solvents.[2,3] This process can be achieved using bifunctional catalysts which contain both acid and metal sites.[4] Acid sites come from a solid support such as alumina, silica and sulfated-zirconia, while the metal sites are facilitated by a supported metal, such as Pt, Pd, Cu and Ni.[3,4]

Experimental/methodology. Bifunctional catalysts were synthesized using sol-gel method for the sulfated-zirconia support and wet impregnation to load Ni. The prepared catalysts were characterized using different techniques such as x-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES), N_2 physisorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), temperature programmed reduction (TPR) and temperature programmed desorption (TPD). Catalytic testing was carried out in an autoclave at 50 bar H_2 pressure and 200 °C using 15 wt% xylitol as the feed.

Results and discussion. TPR confirmed that metal reduction was complete at 400 °C for all catalysts. TPD showed medium to high acid strength and high Ni dispersion on the support surface for the catalysts. Main products observed were ethylene, propylene and butylene glycol, glycerol, methanol and 1- and 2-propanol. An increase in calcination temperature of the catalyst support led to an increase in glycols selectivity.

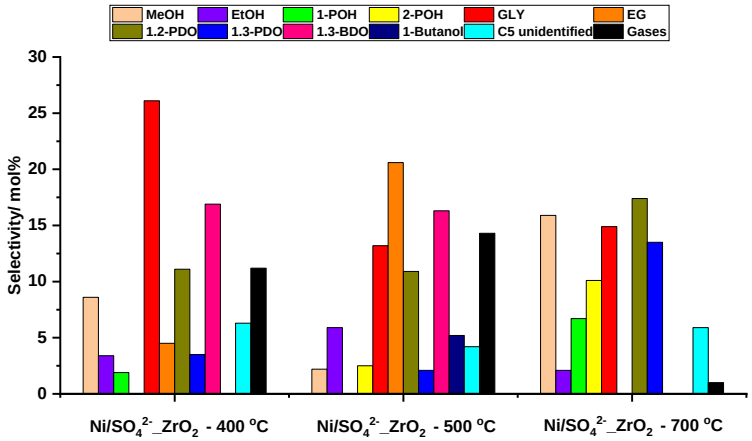

Figure 1: Selectivity of 15 wt.% Ni/SO_4^{2-}-ZrO_2 catalysts at 70% iso-conversion. Reaction conditions: 0.5 g catalyst, 15 wt.% xylitol, 50 bar H_2 pressure.

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Effect of iron on the dispersion of copper on alumina supported catalysts

L. Skuhrovcová[1*], J. Kolena[2]

[1]*ORLEN UniCRE a.s., Ústí nad Labem, Czech Republic*
[*]*lenka.skuhrovcova@orlenunicre.cz*

Keywords: iron, copper, catalysts, surface, support, alumina, hydrogenolysis, glycerol.

Introduction. Selective hydrogenolysis of natural polyols to lower alcohols is a promising way to phase out fossil materials from the petrochemical production system. Copper catalysts are commonly used for the hydrogenolysis of glycerol to 1,2-propanediol, which are a cheaper but less active alternative to noble metal catalysts [1,2]. A new impregnated Cu catalyst, modified with iron was prepared in the frame of this study. Its performance in the selective hydrogenolysis of glycerol to 1,2-propanediol was tested. The effect of iron addition was also studied in detail.

Experimental/methodology. The catalysts were prepared by impregnation with the use of the incipient wetness method followed by drying and calcination. Mesoporous y-alumina was used as the catalysts support, bimetallic water solution of Cu and Fe nitrates was used as the impregnation agent. The catalysts prepared were characterized by following methods: ICP analysis, thermal programmed reduction, X-ray diffraction. N_2 physisorption and SEM microscopy. Testing of the catalysts in the hydrogenolysis of glycerol was carried out in a tubular reactor at a temperature of 230 °C, pressure of 7 MPa with adjustable feed flow rate of hydrogen.

Results and discussion. It was found that a small addition of iron had a considerably positive effect on catalysts activity while the increase of iron amount above Fe/Cu ratio of 0.03 didn't lead to further increase of the activity and even decrease of the activity was observed above Fe/Cu of 0.1. It was disclosed that iron had a positive effect on forming fine dispersion of Cu particles on the catalysts surface and a small amount of iron contributed to the formation of egg-shell Cu profile in the cylindrical catalysts particles at the same time.

Acknowledgments

The work is a result of the project which was carried out within the financial support of the Ministry of Industry and Trade of the Czech Republic with institutional support for long-term conceptual development of research organization. The result was achieved using the infrastructure included in the project Efficient Use of Energy Resources Using Catalytic Processes (LM2018119) which has been financially supported by MEYS within the targeted support of large infrastructures.

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Conversion of biomass-based fructose to organic acid over Sn-MFI and Fe-MFI

N.Sobuś[1*], M. Piotrowski[1], I.Czekaj[1]

[1] *Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Krakow, POLAND*

**natalia.sobus@pk.edu.pl*

Keywords: MFI zeolite; Catalysis; Biomass; Fructose; Lactic acid; Levulinic acid

Introduction

Processing of biomass as a renewable energy source is still a potential alternative solution for the production of energy, fuels and chemicals [1,2]. Out of the three fractions it is composed of, the cellulose fraction is the most energetic [3]. The cellulose fraction is composed of glucose molecules linked by β-1,4-glicosidic bonds [4]. It is possible to decompose it with energy or chemical compounds by grinding, treatment with inorganic acids or with the participation of catalytic materials [5].

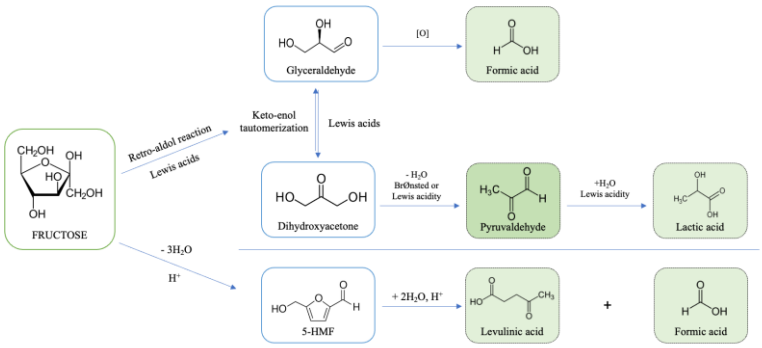

Fig. 1. Valorization of fructose to lactic, formic and levulinic acids.

Experimental/methodology.

MFI-based zeolite catalysts were prepared by ammonium exchange followed by ion exchange using $SnCl_4 \cdot 5H_2O$ and $FeCl_3 \cdot 6H_2O$ salts. The one-pot catalytic conversion of fructose was performed at 220 °C for 1-5 h. Identification of products formed in the post-reaction mixture were identified with the participation of GC

Results and discussion.

Lactic acid (LAC) was obtained with the yield of 68.7% (after 2 h) and levulinic acid (LA) with the yield of 70.9% (after 5 h) with the participation of MFI. In turn, formic acid with a yield of 28.5% (after 5h) was obtained with the participation of Fe-MFI.

Acknowledgments

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Advanced reactor designs for continuous pyrolysis oil conversion into renewable hydrocarbon fuels through hydrodeoxygenation catalysis

A. Søgaard[1], A. P. Krebs[1], M. Z. Stummann[2], M. Høj[1], A. D. Jensen[1*]

[1]*Technical University of Denmark (DTU),*
Department of Chemical and Biochemical Engineering, Kgs. Lyngby, Denmark
[2]*TOPSOE A/S, Kgs. Lyngby, Denmark*
[*] *aj@kt.dtu.dk*

Keywords: sustainable fuels, pyrolysis oil upgrading, catalytic hydrodeoxygenation

Introduction. The transportation sector is a large contributor to anthropogenic climate change, and the demand for green and sustainable technologies for shipping, air and land mobility has progressively increased over the past decades. Electric cars and hydrogen mobility has seen major technological advances and increased commercial availability in recent years. However, for sectors such as aviation and heavy transport, these technologies face many challenges especially regarding energy density. This deems them impractical and unlikely to be cost-effective alternatives to liquid fossil fuels. [1]

Renewable hydrocarbon fuels derived from biomass have recently drawn much attention as more sustainable alternative fuels. They can be easily blended with fossil fuels as drop-in fuels or fully replace in the aviation and heavy transportation sectors. Fast pyrolysis and catalytic fast pyrolysis are two widely applicable and low-cost processes used to convert solid biomass into a condensed bio-oil. [2,3] However, the produced pyrolysis oils are complex chemical mixtures with high water and oxygen contents, which limits their stability and applicability in internal combustion engines. By further upgrading by catalytic hydrodeoxygenation, the properties of pyrolysis oils can be improved significantly, where oxygen is removed through the formation of water with limited negative effect on the carbon yield. [2,4]

In this contribution, we present possible reactor designs for the catalytic hydrodeoxygenation of pyrolysis oils derived from biomass. Two intrinsically different systems are developed and compared to identify the optimal process design and parameters for an efficient, continuous hydrodeoxygenation of pyrolysis oils, and thus the production of sustainable biofuels.

Experimental/methodology. Catalytic HDO experiments have been conducted on two separate reactors: a continuous dual trickle bed reactor setup and continuous slurry type reactor design. The upgraded pyrolysis oils were analysed by high-precision liquid chromatography (HPLC-MS), Karl-Fischer titration for water content and total acid number (TAN) titration. The exhaust gas was analysed by on-line gas chromatography (GC) with a thermal conductivity detector (TCD).

Results and discussion. The dual trickle bed reactor design allowed for treating the pyrolysis oil under a temperature gradient. By introducing an initial stabilisation step at moderate temperatures (180-250 °C) before the hydrodeoxygenation at high temperature (350-450 °C) in the trickle bed reactor, catalyst stability was found to be improved significantly as reactor blockages due to coking was suppressed. Initial results from the slurry type reactor also shows great prospects for efficient hydrodeoxygenation. Research is ongoing to establish the most efficient design for the process.

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Development of continuous reaction system for catalytic dehydrogenation of biomass

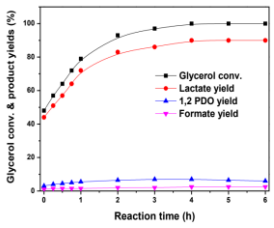
D. Y. Song, J. W. Min, J. H. Kim, I. H. Song*

Korea Research Institute of Chemical Technology, Daejeon, Republic of Korea
**Corresponding Author's E-mail address (*ihsong@krict.re.kr)*

Keywords: Dehydrogenation, CSTR, kinetics, Glycerol

Introduction.
This study aims to produce ethyl lactate from waste glycerol, and separates high purity ethyl lactate through carbonation and esterification. In this process, glycerol and KOH, raw materials, produce potassium lactate through dehydrogenation, and high-purity ethyl lactate is made through esterification with carbon dioxide and ethanol. In this study, we develop the reaction kinetics of glycerol dehydrogenation in order to design a continuous heterogeneous catalytic reactor.

Experimental/methodology.
To develop a reaction kinetics , the mechanism of the catalytic reaction was identified and a high-pressure dehydrogenation reaction was performed to measure the reaction rate of the mechanism. The reaction was conducted in a batch reactor of 1 L with 3%Pt/m-ZrO_2 catalyst 2.1 g, water 140 mL, glycerol 138 g (6M), and KOH 126 g (9M) loaded at the beginning of the operation. N_2 gas was purged at 1 bar and the vapor pressure was observed during the reaction.



	k_ref [L²/mol/gcat/h]	E [J/mol]
k_1	8.34E-03	67329
k_2	1.34E-04	90194
k_3	6.55E-02	40176
	Kad_ref [L/mol]	H [J/mol]
K_G^{ad}	2.90E-02	-2907
K_{KOH}^{ad}	6.43E-02	-2123
$K_{H_2}^{ad}$	3.59E-02	-1735

Results and discussion.
Lactic acid (LA), formic acid (FA), acetaldehyde (AA), and propylene glycol (1,2-PDO; PG) were the main species observed in the experiment, probably due to very fast reaction rates of intermediates. Therefore, the overall reactions were considered for the conversion of glycerol, and the Langmir-Hinshelwood type rate equations were assumed. In the left figure, at 200 °C, glycerol was completely consumed in 4 h of batch time, while the reaction at 180 °C showed approximately 95% conversion, requiring more operating time for the complete consumption. However, the LA yield reached the maximum value of 90% for both temperatures, indicating that there exists a tradeoff for temperature between the batch time and energy consumption. Kinetic parameters were estimated by the aid of the lsqcurvefit function in MATLAB (MathWorks, Inc.) as summarized in the table. And with the kinetics, CSTR reactor was designed by simulation study. It was confirmed that target performance could be obtained by connecting three reactors in series.

Acknowledgments
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Poster Title: Selective cellulose oxidation to formic acid in the presence of vanadium based catalysts

T. Soták*, K. Fulajtárová, D. Gašparovičová, Z. Magyarová, B. Horváth

Institute of Organic Chemistry, Catalysis and Petrochemistry, Slovak University of Technology, Bratislava, Slovak Republic
**tomas.sotak@stuba.sk*

Keywords: cellulose, vanadium-based catalysts, oxidation, formic acid

Introduction.
In recent years, several efficient catalytic systems have been developed to convert cellulose into value-added products. Carboxylic acids including levulinic acid, lactic acid, gluconic acid, acetic acid, and formic acid (FAc) were obtained by transformation of cellulose, glucose or disacharides [1,2]. FAc is an important raw material widely used in the chemical, textile, pharmaceutical, agricultural, and rubber industries. In recent years FAc has been proposed as a reversible source of hydrogen storage, for example for proton exchange membrane fuel cells as a possible hydrogen generator [3]. Currently, the production of FAc is based mainly on fossil resources. Therefore, the production of FAc from biomass can be considered as a promising alternative route to obtain hydrogen from renewable sources [4,5]. In this work, we report on a heterogeneous catalytic system for the oxidation of microcrystalline cellulose to FAc using different supported vanadium oxides as catalysts and water as the solvent.

Experimental/methodology.
Oxidation reactions were carried out in stainless steel autoclaves lined with PTFE at temperature of 200 °C, oxygen pressure of 1.0 MPa for 5 hours. The liquid samples were collected by removing the solid catalyst via centrifugation, and analyzed by HPLC method equipped with UV and RID detectors, using a HPX-87H column and 5 mmol L^{-1} sulfuric acid aqueous solution as the mobile phase with a flow rate 0.5 mL min^{-1}. Contents of carbon dioxide in the gaseous mixtures were determined by GC equipped with TCD.

Results and discussion.

The results of a preliminary study of the cellulose oxidation showed a significant effect of different types of V-based catalysts on the distribution of oxidation products. The highest yield of FAc (65 %) was achieved using a Mo-V/SiO_2 catalyst. These results are similar to those obtained in a reaction system with a difficult to recycle heteropolyacid catalyst (the Keggin-type structure of $H_4PMo_{11}VO_4$). The Mo-V/SiO_2 catalyst was easily separated from the reaction mixture by filtration and used in subsequent runs. Three recyclings of the catalysts proved a good stability of the catalyst in the studied oxidation system.

This catalytic oxidation process promises to be a viable route for the syntheses of formic acid from biomass sources.

Acknowledgments
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Glycerol addition on liquid culture of *Escherichia coli* – evaluation work of microorganisms.

E. Strzelec[1*]

[1]*AGH, University of Science and Technology, Department of Fuel Technology, Cracow, Poland*
[*]*strzelec@agh.edu.pl*

Keywords: biocatalysts, glycerol, *Escherichia coli*

Introduction. Excess of glycerol is an unavoidable by-product in the biodiesel production process. Economic way, ecological solutions and applications for this abundant source of carbon in industry are sought. This poster focuses on the study of the effect of glycerol in the culture of non-metabolized *Escherichia coli* bacteria in a liquid medium.

Experimental/methodology. The number of bacteria was measured using a DEN-1 densitometer (BioSan). *Escherichia coli* bacteria were observed under the microscope before, during and after fermentation. The largest growth of bacteria on the medium with the addition of low and high concentrations of glycerin was obtained after three days, after which this number decreased in most measurements. The production of lactic acid during the growth of *Escherichia coli* bacteria in the lactose broth model medium was monitored by HPLC.

Results and discussion. Based on the obtained results, it can be concluded that unmodified *Escherichia coli* bacteria are a good biocatalyst in glycerol fermentation. One of the fermentation products is lactic acid according to the obtained UV-Vis spectra. HPLC evaluation showed that the *Escherichia coli* had reached the concentration of lactic acid (after 60 hrs fermentation) close to 0,5 g L^{-1}.

As a result, glycerol does not deactivate the bacterial environment, favors the growth of microorganisms, can be converted into organic compounds, and the final compounds obtained are mainly lactic acid.

The proposed process is dedicated to research on the applicability of such solutions in industry (e.g. Orlen company from Poland). The reason for this type of planned research, solutions and proposals for the petrochemical market is also the requirement of a percentage share of bioprocess technology in refineries (biorefineries). In addition, innovation consists in the use of unmodified bacteria and the use of crude glycerol - the omission of the technological process of purification significantly reduces costs. In result, the idea of this project fits perfectly into the Circular Economy policy.

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Ethanol-coupling reactions over MgO, MgO-SiO_2, and MgO-Al_2O_3 catalysts: The effect of promotion by transition metal oxide

B. Szabó[1], Gy. Novodárszki[1], B. Horváth[2], E. Someus[3], D. Deka[4], J. Valyon[1], R. Barthos[1*]

[1]*Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Magyar tudósok körútja 2, Budapest 1117, Hungary*
[2]*Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Ralinského 9, 81237 Bratislava, Slovakia*
[3]*3R-BioPhosphate Ltd., Kajászó, Hungary*
[4]*Biomass Conversion Laboratory, Department of Energy, Tezpur University, Tezpur, India*
[*]*barthos.robert@ttk.hu*

Keywords: ethanol, butanol, butadiene, MgO, MgO-SiO_2, MgO-Al_2O_3,

Introduction. The formation of carbon-carbon bonds is of great importance in chemical technologies. Bioethanol, as a renewable source, can serve as raw material of important chemical products, such as, biofuels and biochemicals. Recently, the heterogeneous catalytic ethanol-coupling reactions, giving 1,3-butadiene (Lebedev reaction) or n-butanol (Guerbet reaction) were receiving special attention. It was proposed that the successive reactions of ethanol take place on a single multifunctional catalyst that either contains spatially separated active sites with hydrogenation/dehydrogenation, C-C coupling and optionally dehydrating activity, or on a catalyst in which ensembles of active sites are able to induce all the mentioned transformations of a 4-carbon activated surface complex.

A common intermediate of the Lebedev and Gourbet reactions is crotyl alcohol. The 1,3-butadiene is formed by dehydration, whereas butanol is obtained by hydrogenation of this intermediate. It is well known that over MgO-SiO_2 and MgO-Al_2O_3 mixed oxide catalysts butadiene and butanol is formed, respectively, with high selectivity. Neat MgO is also known to have a high catalytic efficiency in ethanol coupling, mainly producing butanol and crotyl alcohol. Our present study concerns the role of transition metal oxide additives on the ethanol coupling reactions.

Experimental/methodology. Structure and properties of catalyst preparations was characterized by XRD, STEM, EDS, N2 physisorption. The binding of acidic and basic adsorbates, such as CO2, $CDCl_3$, and NH_3, pyridine, respectively, to the catalyst surface was studied by TPD, and FT-IR measurements. Catalytic reactions were carried out using a fixed bed, continuous flow microreactor at atmospheric pressure. The adsorbed intermediate species formed in the reaction were identified by operando FT-IR measurements.

Results and discussion. Butadiene and butanol were the main ethanol conversion products formed over MgO-SiO_2 and MgO-Al_2O_3 catalysts, respectively, whereas butanol and crotyl alcohol were obtained over pure MgO catalyst. The effect of transitional metal oxide promoters was investigated on the activity of pure MgO. Over Y_2O_3, Ga_2O_3, ZnO, and CuO promoted catalysts the product distribution was similar to that obtained by pure MgO catalyst under identical reaction conditions. However, the conversion was slightly higher due to the Lewis acidic character of the additives and butadiene also appeared among the products. Relative to above mentioned catalysts, promotion of MgO by Nb_2O_5 or Ta_2O_5 resulted in higher dehydrogenating activity, and high butadiene selectivity, while the formation of butanol and crotonaldehyde was suppressed. High acetaldehyde selectivity showed that In_2O_3 promoter increased dehydrogenation activity. The modification ZrO_2 strongly enhanced dehydration, bringing about high butadiene and ethylene selectivities.

Catalytic test reactions using promoted mixed oxides are in progress, as well as, reactions of possible intermediates, and their mixtures.

Acknowledgments

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Kinetic study on fatty alcohols synthesis by homologation of ethanol with methanol

A. Takahashi*, K. Sugahara, T. Chida, K. Hiromori, N. Shibasaki-Kitakawa

Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, Sendai, 980-8579, Japan
**Corresponding author: atsu4.t@tohoku.ac.jp*

Keywords: Fatty alcohol synthesis, homologation, ethanol

Introduction. C1-C6 aliphatic alcohols have diverse applications depending on their carbon chain length and structure and isobutanol has recently attracted attention for its properties as a drop-in fuel. Therefore, production of these fatty alcohols from renewable resources leads to realization of biorefinery. We have proposed a method to upgrade to desired C3 or higher (C3+) alcohols by using ethanol (EtOH) as a base feedstock and methanol (MeOH) as an homologation feedstock. Previously, we found that C3 or iso-C4 alcohols are produced by using Cu/ZrO_2 catalyst[1]. In this study, we clarified the reaction mechanism based on a kinetic model analysis to understand the catalyst design guidelines for upgrading to C3+ alcohols.

Experimental/methodology. The catalyst, 5 wt% Cu/ZrO_2, was reduced with H_2+Ar gas before the reaction as an activation process. In the synthesis experiment, the feedstock was vaporized, mixed with Ar, and fed to the catalyst bed set at 300°C at a given concentration. As operating factors, the MeOH/EtOH molar ratio was varied from 0-5 and the contact time (W/F) from 0.01-0.04 g·min/cm^3-cat. In each experiment, the component concentrations in the effluent gas were measured by on-line GC-TCD. The carbon-based yield Y_i of component i was then calculated from the measured values at steady state.

Results and discussion. The kinetic model for the synthesis of C3+ alcohols from EtOH is based on the following reaction mechanism. A schematic diagram of the reaction mechanism considered is shown in Fig. 1. In the case of EtOH alone (a), the dehydrogenation of EtOH (step 1) is followed by aldol condensation of acetaldehyde(C2) (step 2) to form n-C4 aldehyde (n-C4 ald.) and subsequent hydrogenation (step 3) to form n-C4 alcohol (n-C4 alc.)[2]. The formation of ethyl acetate (EA) (step 4) was considered as a side reaction. Next, in the case of EtOH+MeOH (b), the aldol condensation and hydrogenation of C2 with MeOH was considered to result in the homologation and branching of the carbon chain from n-C3 species to iso-C4 species (steps 5-8). In addition, further homologation (step 9) was also considered. As side reactions, the formation of methyl acetate (MA) from C2 (step 10) and the formation of CO and CO_2 from MeOH (steps 11 and 12) were also considered. In addition, the formation of acetic acid (C2 acid) and crotyl alcohol (Cro. alc.) (steps 13, 14) were also considered[3,4]. The formation of alc. by direct coupling of EtOH or EtOH with MeOH was also considered (steps 15-18) since the parallel formation of alc. and ald. was observed in the experiments on the effect of W/F. The reaction in each step is assumed to follow the Langmuir-Hinshelwood mechanism and the model equation was derived. The model constants were estimated by fitting the experimental results at varied MeOH/EtOH ratio and W/F.

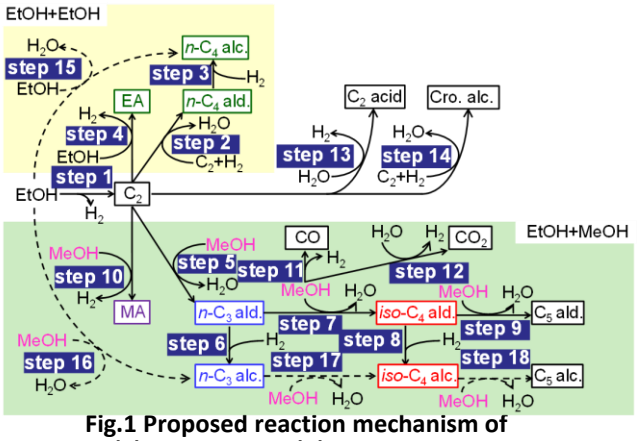

Fig.1 Proposed reaction mechanism of (a)EtOH + EtOH, (b)EtOH + MeOH

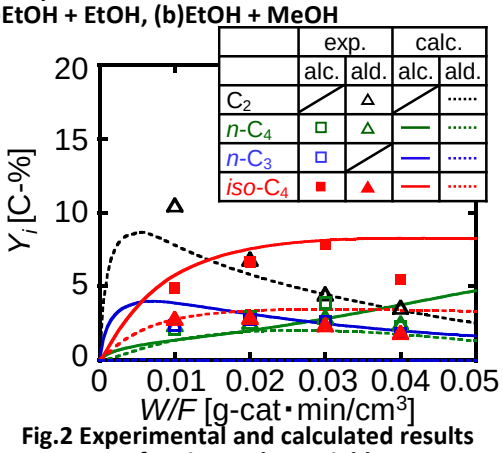

Fig.2 Experimental and calculated results of main products yield

Fig. 2 shows the effect of W/F on the main product yield at MeOH/EtOH=2. The calculated results (line) are in good agreement with the experimental results (plot), indicating that the reaction mechanism was captured by the model.

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Aldol condensation of furfurals with acetone: challenges and opportunities

A. Tampieri[1,2], N. Barrabés[1], F. Medina[2], K. Föttinger[1*]

[1]*Institute of Materials Chemistry, Technische Universität Wien, Vienna, Austria*
[2]*Chemical Engineering Department, Universitat Rovira i Virgili, Tarragona, Spain*
[*]*karin.foettinger@tuwien.ac.at*

Keywords: Aldol condensation, hydrotalcite, *in situ*/*operando*, ATR-IR, NMR.

Introduction. In response to the environmental changes due to the utilization of fossil fuels for the production of energy and chemicals, biomass has been proposed as an alternative and sustainable raw material. Bio-derived furanic aldehydes such as furfural and 5-hydroxymethylfurfural (HMF) can undergo aldol condensations with acetone to yield condensation products with higher carbon numbers that are precursors to renewable hydrocarbon fuels, polymeric materials and dyes [1]. Much research has focused on heterogeneous catalysts; in this regard, Mg:Al hydrotalcites and derived solids proved to be premium aldol condensation catalysts [2]. The use of heterogeneous catalyst could facilitate the purification processes, and they could be designed to drive the selectivities; however, the high oxygen content of bio-derived molecules and the presence of multiple unsaturations promotes the establishment of strong interactions with the catalytic surface, which may lead to deactivation [3].

Experimental/methodology. The parent Mg:Al hydrotalcites were synthesised via the coprecipitation method; the hydrotalcites were calcined to obtain the corresponding mixed metal oxide; this solid was immersed in pure water to obtain the rehydrated hydrotalcite. Our previous work includes extensive characterisation of the catalysts [3], while the present work focuses on the use of FT-IR and UV-Vis. The catalysts were tested in the neat liquid-phase aldol condensation of furfurals with acetone in a round bottom flask, and the collected liquid samples were analysed by GC-FID. Online and *in situ*/*operando* ATR-IR and in situ NMR were also used to study the catalytic system under operation.

Results and discussion. The results of the catalytic tests of the cross-condensations and of the self-condensation of acetone allowed the comparison of the different reactivity of the two aldehydes. These results, together with the spectroscopic studies of the liquid and/or solid phases, were used to gather insights into the reaction and deactivation mechanisms. Online and *in situ*/*operando* ATR-IR was used to monitor the reaction over time and to study the interaction of the reaction species with the solid catalyst, especially the formation of deactivating organic matter that covers the surface. *In situ* NMR was used to study the ongoing reaction, assessing its stereoselectivity, and to study the reaction of deuterated species in the catalytic system, shedding light on the behaviour of elusive intermediates. NaOH was also used as a catalyst to gather additional mechanistic information.

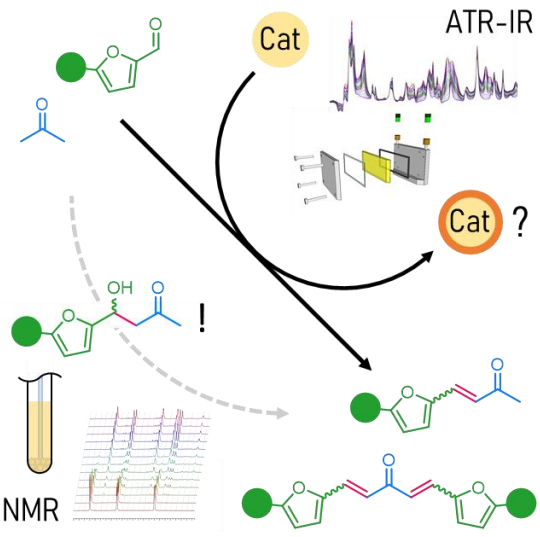

Figure 1. Aldol condensation of furfurals with acetone, and main findings.

Acknowledgments

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Utilizing Deep Eutectic Solvents (DES) for the Enhanced Production of 5-Hydroxymethylfurfural and Furfural from Biomass in Innovative Multiphase Systems

N. Thanheuser,[a,c] J. Esteban,[b] A. J. Vorholt,[a] W. Leitner [a,c]

[a]Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany; [b]Department of Chemical Engineering, The University of Manchester, Manchester, United Kingdom; [c]Institut für Technische und Makromolekulare Chemie, RWTH Aachen, Aachen, Germany.

Keywords: Biomass, Multiphase Catalysis, 5-Hydroxymethylfurfural, Furfural; Deep Eutectic Solvents

Introduction. Owing to fossil-based resource depletion, the valorization of lignocellulosic biomass derived sugars has gained more interest for the production of chemicals. 5-hydroxymethylfurfural (HMF) and furfural are highly valued building blocks that can be obtained by the dehydration of glucose, fructose and xylose. To prevent the formation of undesired side reactions that occur in monophasic aqueous systems, a multiphase approach can be followed, whereby a reaction with *in situ* extraction takes place, utilizing the concept of process intensification .[1,2] With regard to Green Chemistry, the choice of solvents is a matter of interest. Therefore, environmental, health and safety (EHS) as well as the performance of the chosen solvent have to be considered. Several solvent selection guides have been established taking the EHS parameters into account.[3] To assess the performance, the Conductor-like Screening MOdel for Real Solvents (COSMO-RS) is a proven tool for screening different candidates based on structural information of the molecules. COSMO-RS screenings among a pool of selected solvent candidates gave methyl propionate and ethyl acetate as best performing extraction phases. As for the reaction phase, even though water provides a safe and productive reaction medium, it promotes the unwanted ring opening rehydration of HMF to formic and levulinic acid and self-condensation leading to undesired polymers and humins.[4]

DES are formed by the combination of a hydrogend bond acceptor (HBA) and donor (HBD), amongst being classified as green solvents, provide a higher selectivity towards HMF and suppress rehydration of the product thus by-product generation. The formation of DESs with acidic HBDs (e.g. carboxylic acids) initiates the acid catalyzed dehydration reaction. Applied in a biphasic reaction approach, which provides easier product separation, they potentially improve yields and selectivity towards HMF.

Experimental/methodology. In a biphasic system with MIBK as extracting phase, dehydration reactions were performed undermicrowave irradiation with ethylene diaminetetraaceticacid (EDTA) as a catalyst due to its thermomorphic behaviour at temperatures above 140 to 170 °C. Dehydration reactions employing DESs in a biphasic system were carried out under reflux between 80 and 100 °C.

Results and discussion. For an aqueous reaction phase, MIBK shows a promising performance with the advantage of not undergoing hydrolysis under the typical acidic conditions of the reaction compared to methyl propionate and ethyl acetate. The modification of the reaction phase to DESs, resulted in an almost complete suppresion of by-product formation. The best result Y_{HMF}= 51 %; $X_{Fructose}$ = 92 %; S_{HMF}= 55 % was observed at 80 °C after 0.5 h with no formation of formic and levulinic acid as well as no formation of solid by-products (humins). Since the partition coefficients observerd for HMF and Furfural were not as high as in the case of aqueous biphasic systems, a COSMO-RS solvent screening for the extraction of HMF from Choline-Chloride:Oxalic acid DES was performed. *α*-pinene and *n*-heptane were experimentally tested due to their high ranking in the predictions, but extraction performance compared to MIBK proved worse. However, acetonitrile is a promising extraction agent,[5] which in combination with a self-consuming DES system made of ChCl and various C6 and C5 carbohydrates, offers a possible reaction system.

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Bimetallic Based Catalysts for Base-Free Oxidation of Furfural: High-throughput experimentation studies

J. Thuriot-Roukos[1], C. P. Ferraz[1], S. Heyte[1] , S. Paul[1] and R. Wojcieszak[1*]

[1]*Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181-UCCS-Unité de Catalyse et Chimie du Solide, F-59000 Lille, France*

[*]*robert.wojcieszak@univ-lille.fr*

Keywords: biomass valorisation, furfural oxidation, high-throughput experimentation

Introduction. Reducing the carbon footprint of chemical industries involves the use of biobased compounds, such as furfural (FF) which is a renewable platform molecule[1]. Base-free oxidation of FF using metal catalysts is a sustainable approach to produce furoic acid (FA) and maleic acid (MA)[2]. In this study, bimetallic Au_xPt_y and Au_xPd_y catalysts with different metals ratios supported on TiO_2 were tuned to provide experimental evidence for the modulation of their selectivity to FA and MA in FF conversion.

Experimental

Bimetallic systems have been synthesized using the REALCAT high-throughput platform, by applying a DoE methodology (central composite design) to study 2 different parameters (metal loading and metals ratios) on the selectivity of the FF oxidation reaction. All catalysts were characterized using different techniques such as Inductively coupled plasma (ICP) and X-Ray Diffraction (XRD). Furfural oxidation tests using the bimetallic catalysts were carried out on the REALCAT platform in a Screening Pressure Reactors system (SPR) from UnchainedLabs.

Results and discussion.

The selectivities of Au_xPt_y and Au_xPd_y bimetallic systems supported on TiO_2 with different molar ratios (1:3, 1:1, and 3:1) and metal loading (0.5, 1.25, and 2%) in the various products of oxidation of furfural are shown on Figure 1 at isoconversion of FF (around 30%). The products distribution changed significantly depending on the composition of the catalytic system[3]. Au-Pd systems were found to generally exhibit a higher selectivity towards FA than Au-Pt systems. Gold-rich catalysts promote the oxidation of FF to FA and MA selectivity is dependent on the amount of Pt or Pd.

Studying the composition and the structure of the Au-Pd and Au-Pt bimetallic catalysts is a key factor for designing more active catalysts and to find the relationships between their structures and their catalytic performances.

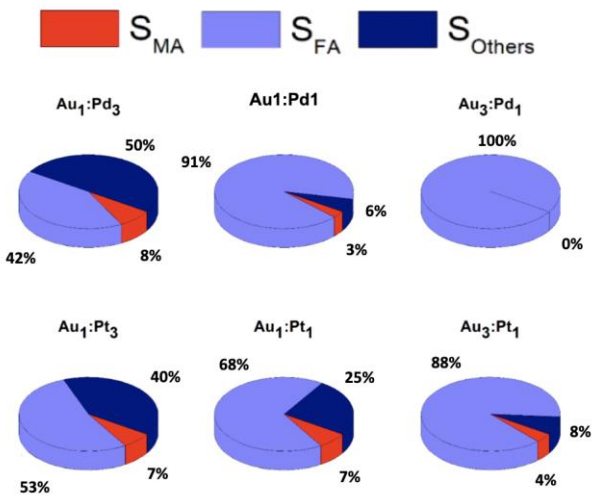

Figure 1 : Selectivity charts for the bimetallic catalysts (at similar conversions, 30%)

Acknowledgments

The REALCAT platform benefits from a state subsidy administered by the French National Research Agency (ANR) within the frame of the 'Future Investments' program (PIA) with the contractual reference ANR-11-EQPX-0037. The European Union, through the ERDF funding administered by the Hauts-de-France Region, has co-financed the platform. Centrale Lille, the CNRS, and Lille University, as well as the Centrale Initiatives Foundation, are thanked for their financial contributions to the acquisition and implementation of the equipment of the REALCAT platform. The Chevreul Institute (FR 2638) and the Ministère de l'Enseignement Supérieur, de la Recherche, et de l'Innovation are also acknowledged for supporting and partially funding this work.

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Oxidative cleavage of vicinal diols over Fe/MFI: correlation of Fe speciation with catalytic activity

P. Treu[1*], B. B. Sarma[1,2], J.-D. Grunwaldt[1,2], E. Saraci[1,2*]

[1]*Institute of Catalysis Research and Technology, KIT, Eggenstein-Leopoldshafen, Karlsruhe, Germany*
[2]*Institute for Chemical Technology and Polymer Chemistry, KIT, Karlsruhe, Germany*
**philipp.treu@kit.edu, erisa.saraci@kit.edu*

Introduction. Oxidative cleavage of vicinal diols where each carbon is oxidized to an aldehyde or carboxylic acid is an attractive way of upgrading bio-derived polyols [1]. Supported monomeric Fe catalysts, in particular, have shown efficiency in the oxidation of methane [2] while also being a comparatively cheap, benign and sustainable heterogeneous catalyst material. Here, we show the unprecedented use of Fe/MFI catalysts in the oxidative cleavage of C–C bonds of ethylene glycol (EG) as model compound in biomass derived platform molecules.

Experimental/methodology. Catalysts with different Fe-loadings were prepared *via* incipient wetness impregnation. UV-Vis in combination with electron mircroscopy (STEM), X-ray absorption spectroscopy (XAS) and N_2-physisorption were used to study the Fe-speciation on the zeolite support. Catalytic activity tests were used to derive structure-activity relationships, elucidating the active site of the catalyst.

Results and discussion. Up to a loading of 0.5 wt% monomeric Fe-sites are the dominating Fe-species, while at higher loadings an increasing amount of oligomeric and even bulk Fe_2O_3 can be observed (Figure 1a). Additionally, the reaction rate of the oxidative cleavage of EG increased linearly with to 0.5 wt% Fe then it leveled out for higher Fe-loadings (Figure 1b, black plot), while the turnover rate (TOR) decreases steadily with increasing Fe-loading (Figure 1b, red plot). The correlation between the nature of the Fe-sites and activity can be seen in Figure 1c, where the TOR is plotted against the relative amounts of monomeric and oligo+bulk species. Notably, the monomeric Fe-sites are responsible for the increasing TOR of the reaction, while oligo+bulk Fe-species have no major contribution to the catalytic activity and may even be detrimental. These results demonstrate that the optimal catalyst for the heterogeneously catalyzed EG cleavage should have well distributed monomeric Fe-sites and no/minimal amount of oligomeric/bulk Fe species [3]. In addition, investigation of the active Fe-species using operando XAS measurements show the state of the catalyst under reaction conditions, further underlining the importance of monomeric Fe-species**.** Bulkier molecules containing vicinal diol groups were also tested showing the relevance of Fe/MFI catalysts for this reaction, providing new capabilities the valorization of biomass *via* oxidative cleavage.

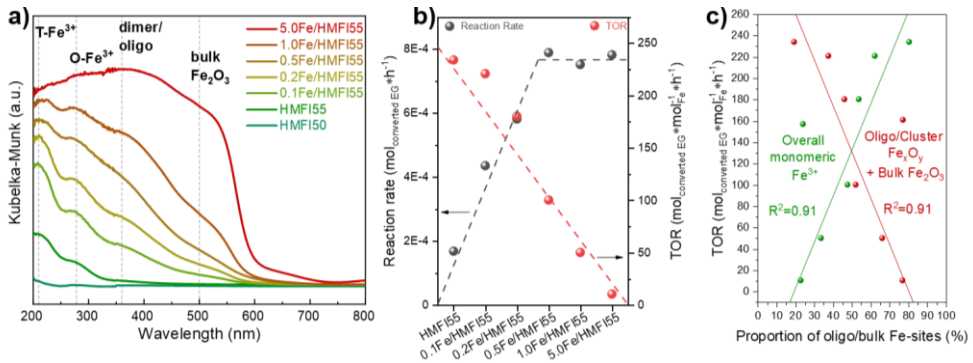

Figure 1. a) Diffuse reflectance UV-vis spectra of Fe/HMFI55 catalysts. Absorption wavelength positions of various Fe-species are shown by the dotted lines. b) Reaction rate and TOR of HMFI55 with varying Fe-loading. Dashed lines are provided to guide the eyes. Reaction conditions: n_{EG}=0.715 mmol; $n_{H_2O_2}$=3.6 mmol; V_{H_2O}=10 ml; m_{cat}=100 mg; T=323 K. k has been calculated at interpolated reaction time for X=50%. c) Positive and negative correlation between TOR and relative amount of monomeric and oligomeric/bulk Fe-species, respectively.

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Biogas reforming on solution combustion synthesis catalysts

S. Tungatarova[1,2*], A. Manabayeva[1,3], D. Murzin[4], P. Mäki-Arvela[4], T. Baizhumanova[1,2]

[1]*D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan*
[2]*Al-Farabi Kazakh National University, Almaty, Kazakhstan*
[3]*Kazakh-British Technical University, Almaty, Kazakhstan*
Laboratory of Industrial Chemistry and Reaction Engineering, ÅboAkademi University, Turku, Finland
[*]*Corresponding Author's E-mail address: tungatarova58@mail.ru*

Keywords: methane, hydrogen, reforming, nickel

Introduction. In recent years, the world has begun an intensive study of processes involving biogas as an alternative source of not only energy, but also raw materials for petrochemical production due to the inevitable depletion of non-renewable energy sources and raw materials for petrochemical production. Biogas, resulting from the anaerobic fermentation of biomass and any organic waste, is a practically inexhaustible renewable resource for obtaining valuable products such as hydrogen, synthesis gas and hydrocarbons.

Experimental/methodology. The results of carbon dioxide reforming of CH_4 (model biogas) on the Ni-Co-Mg-Ce catalysts prepared by solution combustion synthesis (SCS) and impregnation of moisture capacity methods were compared. The studies were carried out at various space velocities, temperatures, composition of the reaction mixture and other parameters. CH_4 and CO_2 diluted with an inert gas (Ar) in the presence and absence of water vapor was used for reforming.

Results and discussion. Dry reforming of methane was studied at GHSV = 860 h^{-1} and the ratio of the components of the reaction mixture $CH_4 : CO_2 : Ar = 33.3 : 33.3 : 33.3$ as well as at GHSV = 2500 h^{-1} when the ratio of the components of the mixture of $CH_4 : CO_2 : Ar = 46.7 : 23.3 : 30.0$. Figure 1 shows the effect of space velocity and the addition of water vapor on the conversion of raw materials and the yield of reaction products. It can be seen from the figure that when the space velocity decreases from 2500 h^{-1} to 860 h^{-1}, the CH_4 conversion, the yields of H_2 and CO increase, and the addition of water vapor further increases the conversion of the feed and the yield of H_2.

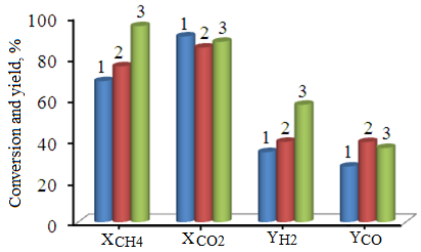

Fig. 1. The effect of space velocity and the addition of water vapor on the conversion of raw materials and the yield of reaction products. 1 - 2500 h^{-1} – H_2O, 2 - 860 h^{-1} – H_2O, 3 - 860 h^{-1} + H_2O

Similar experiments were carried out on the same composition of the catalyst, prepared by the method of impregnation by moisture capacity at space velocities of 860 and 2500 h^{-1} at 850 and 900°C in the presence and absence of water vapor. Comparative results show that the preparation of catalyst by impregnation is inferior to the SCS method, in which higher values of feed conversion and H_2 yield are obtained. As a result of the temperature change, it was found that carrying out the process at 900°C allows one to achieve high values of both yield and selectivity for H_2 and CO, but the H_2/CO ratio decreases from 6.1 (T = 700°C) to 3.9 (T = 900°C) at GHSV = 2500 h^{-1}. The characteristics of the catalysts by BET, XRD, TEM, SEM, TPD methods were determined and the features of the synthesis of spinels and metal alloys, which play a decisive role in the activation of the samples, were analyzed.

Acknowledgments
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Acidity efffects on the NiCu catalyzed hydrodeoxygenation of 4-(2-Furyl)-3-buten-2-one

T. Vandevyvere [1;2], M. K. Sabbe [1;2], J. W. Thybaut[2], D. Kubička[3], J. Lauwaert[1,*]
[1]Industrial Adsorption and Catalysis Technology, Ghent University, Ghent, Belgium
[2]Laboratory for Chemical Technology, Ghent University, Ghent, Belgium
[3]Department of Petroleum Technology and Alternative Fuels, University of Chemistry and Technology Prague, Prague, Czech Republic
[*]*Jeroen.Lauwaert@UGent.be*

Keywords: Furfural, aldol condensation, hydrodeoxygenation, NiCu, SiO_2, γ-Al_2O_3, SIRAL 1

Introduction. Furfural is a platform molecule which can be obtained from dehydration of biomass-derived sugars, and is expected to play a vital role in future biorefineries [1]. In a promising route to produce diesel and jet fuels, for example, furfural condensation with acetone is performed to produce species with adequate carbon numbers, 4-(2-Furyl)-3-buten-2-one (FAc) being one of the main products. Subsequent hydrodeoxygenation (HDO) of the condensation products results in a blend of stabilized molecules with improved energy density. However, the used HDO catalyst should be able to transform a variety of moieties, i.e. furan rings, unsaturated bonds and carbonyl groups, which is challenging. Prior work has shown that the utilization of acid sites at mild HDO temperatures is crucial to achieve a complete removal of the oxygen moiety and to induce ring opening, but can lead to coking as well [2,3]. Moreover, the use of NiCu has been found to be effective in the hydrogenation of these biomolecules [3]. An investigation is, however, yet to be performed on the acidity effects of NiCu catalysts in FAc HDO at mild conditions. In this work the support used for the NiCu catalyst is systematically varied from non-acidic to mildly acidic and the effects on hydrogenation, hydrodeoxygenation, ring opening and coking are assessed.

Experimental/methodology. The catalysts were synthesized using incipient wetness impregnation of the metal precursors: $Ni(NO_3)_2.6H_2O$ and $Cu(NO_3)_2.3H_2O$ on SiO_2, γ-Al_2O_3 and SIRAL 1. Ni and Cu (ratio Ni/Cu = 1/1 mol/mol) were added in 20 wt%. Hereafter, the catalysts were calcined at 450 °C for 4 h. The catalysts were characterized via N_2- sorption, NH_3-TPD, H_2-TPR, XRD, XPS and TEM-EDX. The catalyst performance was assessed in a 300 mL high-pressure batch reactor. 1 g of 4-(2-Furyl)-3-buten-2-one and 150 mL of solvent was loaded into the reactor. The system was then heated up to the desired reaction temperature and pressurized with H_2 under slow stirring speed (100 rpm). Once the reaction conditions were reached, the stirring speed was set to 1000 rpm, and the start time was noted. Samples were taken at regular time intervals during the course of reaction.

Results and discussion. The effect of acid sites on the reaction mechanism of FAc HDO has been elucidated. The necessity of support acidity is clear, since the SiO_2 supported catalyst could practically only hydrogenate FAc. A bifunctional catalyst is thus necessary at mild HDO conditions where metal sites hydrogenate the reactant and acid sites break the C-O bond. Preliminary results have shown that stronger acid sites however result in more coking. The best performing catalyst is further used to optimize the reaction conditions to maximize the yield of hydrocarbons.

Acknowledgments
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Biogas reforming over Ni supported on hierarchical zeolites: The effect of biogas composition and O_2 co-feeding

Amanda de C. P. Guimarães[1], Andressa A. A. Silva[2], Rita de C. C. Simões[2], Cristiane A. Henriques[1], Lisiane V. Mattos[2*]

[1]*Rio de Janeiro State University, Institute of Chemistry, Graduate Program in Chemical Engineering*
[2]*Federal Fluminense University, Department of Chemical Engineering*
**lisianemattos@id.uff.br*

Keywords: Dry reforming, biogas, hierarchical zeolites.

Introduction. Biogas presents high levels of CO_2, resulting in emissions into the atmosphere that contribute to the greenhouse effect increase. The conversion of biogas into synthesis gas by CO_2 reforming of methane (DRM – dry reforming of methane) has been considered a promising alternative for obtaining products with a higher added value, such as H_2. Ni-based catalysts have been extensively studied for the DRM due to their low cost and high activity, but this metal is prone to coking. The nickel particle size significantly affects the nucleation rate of carbon. Thus, one approach to minimize carbon formation is to control metal particle size and avoid metal sintering by using support with a high surface area, such as zeolites. Catalysts supported on zeolites are widely used due to their unique properties, such as high thermal stability and uniform microporosity. The use of hierarchical zeolites, obtained from desilication and dealumination/desilication processes, promote the increase of mesopores to increase the accessibility of pores and active sites and confine metallic nanoparticles. Therefore, catalysts supported on hierarchical zeolites have been identified as promising for biogas reforming. Adding oxygen to the feed can also avoid carbon formation and decrease the energy input required in the reformer since the partial oxidation of methane is an exothermic reaction. Moreover, fluctuations in the biogas composition can affect the catalysts' performance, which depends on the organic matter. Then, this work aims to study the effect of feed composition on the performance of Ni (1 and 3 wt.% of Ni) supported on ZSM-5 and USY zeolites with a hierarchical porous system during DRM.

Experimental/methodology. ZSM-5 zeolite was desilicated with sodium carbonate to form mesopores [1], while USY zeolite underwent two subsequent treatments, dealumination with H_4EDTA and desilication with sodium hydroxide and TPAOH to form the hierarchical structure [2]. The catalysts were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and nitrogen adsorption. DRM was carried out at 1073 K with a 1:1 CH_4/CO_2 molar ratio during 24 h time on stream (TOS). The catalyst with the best performance was also tested at a 1.5:1 CH_4/CO_2 molar ratio and 1.5:1:0.25 $CH_4/CO_2/O_2$ molar ratio.

Results and discussion. The X-ray diffractograms of the catalysts are similar to that of the respective parent zeolite, showing that the treatments performed did not cause the structure collapse. For both zeolites, no significant changes were observed in the volume of micropores after the alkaline treatments. However, the results showed that the alkaline treatment caused an increase in mesoporosity compared to the parent zeolites. Besides, the ZSM-5 zeolite has a greater volume of mesopores than the USY. The values of initial methane and CO_2 conversions were slightly higher for the desilicated 3Ni/ZSM-5, but all samples presented a deactivation during the reaction. Comparing the catalysts supported on zeolite of the same topology, the increase in Ni content and volume of mesopores led to an increase in the catalytic activity. With increasing CO_2 concentration in the feed, the H_2/CO molar ratio slightly decreases due to the reverse Boudouard reaction. Thus, at a CH_4/CO_2 molar ratio of 1.5, H_2 selectivity is favored. The addition of O_2 to the feed increased the H_2/CO molar ratio from 0.66 to 1.0. Furthermore, the presence of O_2 improved the catalyst stability during 24 h TOS for DRM. This increase in stability was likely due to the lower carbon formation.

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Dry reforming of methane over Ni supported on desilicated ZSM-5 zeolites: The effect of alkaline treatment conditions and Si/Al ratio

Lícia R. F. Coelho[1,2,4], Andressa A.A. da Silva[4], Raimundo C. R. Neto[2] , Fábio B. Noronha[1,2,3]
Lisiane V. Mattos[4*]

[1]Dept de Engenharia Química/Instituto Militar de Engenharia 22290-270 (Brazil)
[2]Instituto Nacional de Tecnologia 20081-312 (Brazil)
[3]University of Lille, Lille, (France)
[4]Fluminense Federal University, Niterói 24210-240 (Brazil)
**lisianemattos@id.uff.br*

Introduction. Ni-based catalysts have been studied for the DRM due to its low cost and high activity but Ni is prone to coking, with carbon formation being favored in large Ni particles. Thus, new preparation methods have been proposed in the literature aiming at a better control of the Ni particle size during the DRM reaction and, consequently, an improved resistance to carbon deposition (1). The desilication of MFI-type zeolites has been shown to be an efficient post-synthesis method for generating mesoporosity by preferentially removing Si from the interior of the crystals through the use of an alkaline solution. These new structures could maintain the metallic particles confined, preventing their sintering (2). Therefore, the main objective of this work is to evaluate the effect of alkaline solution concentration and Si/Al ratio on the performance of Ni catalysts supported on desilicated HZSM-5 zeolites for DRM.

Experimental/methodology. A series of commercial ZSM-5 zeolites with different SiO_2/Al_2O_3 molar ratio (23, 50, 80, 280, Zeolyst) were used as supports. The zeolites were calcined under N_2 at 525°C for 12h. The catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ in order to obtain 1 wt % of the metal. The fresh catalysts were treated with an aqueous solution of Na_2CO_3 at two different concentrations, 0.3 and 0.6 mol/L, at 80 °C for 12h (3). Then, all samples were reduced under H_2 atmosphere at 800°C for 30min. The desilicated samples will be designed as Ni/ZX_Ydsc, where X is the SiO_2/Al_2O_3 molar ratio and Y is the concentration of Na_2CO_3. The catalysts were characterized by N_2 adsorption, XRD, SEM, TEM and TGA. DRM was carried out at 800°C, using a CH_4:CO_2 molar ratio of 1.0.

Results and discussion. The N_2 adsorption/desorption isotherms results revealed that the desilication treatment led to an increase in the mesoporosity of the samples with the appearance of a hysteresis loop for the desilicated catalysts. Increasing the concentration of alkaline solution increased the mesopourous volume for all samples. For the samples treated with the 0.6 mol/L $NaCO_3$ solution, the volume of mesopourous decreased in the following order: Ni/Z280_0.6dsc >Ni/Z80_0.6dsc >Ni/Z50_0.6dsc >Ni/Z23_0.6dsc. This result showed that the increase of the Si/Al molar ratio favored the formation of mesoporosity. For untreated samples, Ni/Z280 and Ni/Z80 exibited the highest methane conversion during DRM. However, these catalyst underwent a continous deactivation during 24 h time on stream (TOS) for DRM, while the CH_4 conversion remained constant for Ni/Z50. Ni/Z23 showed no activity. The desilication treatment improved the methane conversion, which was more significant for the samples treated with the 0.6 mol/L $NaCO_3$ solution. Ni/280_dsc exhibited the highest value of methane conversion and remained quite stable during 24 h of TOS. These results indicate that the use of a higher alkaline solution concentration and higher Si/Al ratio improved the performance of the catalysts. This is likely due to the higher mesoporosity formed, which could contribute to the confinement of the metallic particles, avoiding its sintering.

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Comparison between the crystalline phases of ZrO_2 in methyl levulinate reduction to γ-valerolactone: a theoretical and experimental study

Alessia Ventimiglia[1], Riccardo Bacchiocchi[1], Nikolaos Dimitratos[1], Ivan Rivalta[1], Tommaso Tabanelli[1*]

[1]*Dipartimento di Chimica Industriale "Toso Montanari", University of Bologna, Viale del Risorgimento 4, 40136-Bologna, Italy*

[*]*tommaso.tabanelli@unibo.it*

Keywords: GVL, biomass, DFT, H-transfer

Introduction. Zirconia (ZrO_2) is a polymorphic oxide present in different allotropic forms; thanks to its amphoteric properties, ZrO_2 is used as support for heterogeneous catalyst or as catalyst itself; in particular, it is used in hydrogenation, oxidation and isomerization processes[1]. Its ability to promote the H-transfer reaction by using alcohols as H-donor in the reduction of levulinic acid derivatives to γ-valerolactone (GVL) has been studied recently[2]. In particular, reduction of Methyl levulinate (ML) using ethanol as H-donors in gas-phase is presented in this work. First, there is a cyclization of ML, with the formation of the intermediate angelica lactones (ALs); subsequently, the double bond is hydrogenated by H-transfer, leading to the formation of the final product, GVL**.** Herein, an investigation and comparison of two different crystalline phase zirconia catalysts with a similar specific surface area, a tetragonal (*t*-ZrO_2) and a monoclinic (*m*-ZrO_2) one, is reported. Indeed, these two zirconia phases possess differing symmetry and a differing coordination of the exposed suface atoms, leading to different catalytic activity. **Experimental/methodology.** The catalysts were synthesized by precipitation for *t*-ZrO_2 and hydrothermal for the *m*-ZrO_2 and then characterized in order to evaluate their crystallinity, surface area and the number of Lewis acid and basic sites. Finally, they were tested in the H-transfer reaction of ML to GVL in a continuous gas phase reactor using ethanol as H-donor. In order to better understand its catalytic properties, a computational study based on density functional theory and atomistic modeling of ZrO_2 clusters of the two crystalline phase under study was performed[3]. **Results and discussion.** *t*-ZrO_2 has proven to be a suitable catalyst for this reaction: indeed, it is selective toward the formation of GVL (yield 70%). However, by carrying out the reaction under the same conditions with *m*-ZrO_2 catalyst, the catalytic activity was reduced and deactivation was observed (Figure 1).

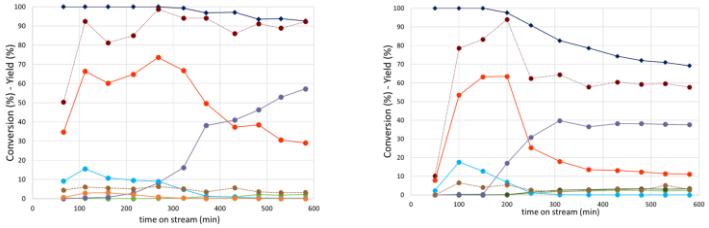

Figure 1. ML reduction using EtOH as H-donor over t-ZrO2 (left) and m-ZrO2 (right).Reaction conditions: molar ratio ML:EtOH=1:10, T=250 °C, t=1 s, %mol N_2:ML:EtOH=90.1:0.9:9. Conversion (◆); EL (●); GVL (●); Ethyl GVL (●); aAL (●); bAL (●); Others (●); Yields sum/Conversion (●).

To understand the faster deactivation of *m*-ZrO_2 when compared to *t*-ZrO_2, we focused on the adsorption of the intermediate of the reaction, ALs, on the two phases. Indeed, one of the possible reasons for the different reactivities of the two crystalline phases is the deactivation of the catalyst by formation of heavy products that block the catalytically active surface sites[4]. The computational results clearly show the stronger interaction of ALs with *m*-ZrO_2 phase respect to *t*-ZrO_2, which leads to a higher formation of oligomers, thereby promoting surface deactivation.

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Synthesis of Templated Mesoporous Sulfonic Carbons for the Conversion of Fructose and Xylose into Platform Molecules

J. L. Vieira[1], M. J. Pinzón-Cárdenas[2], E. A. Santos[2], J. M. R. Gallo[1*]
[1]*Federal University of São Carlos, São Carlos-SP, Brazil*
[2]*State University of Campinas, Campinas-SP, Brazil*
[*]*jean@ufscar.br*

Introduction. The platform molecules 5-hydroxymethylfurfural (HMF) and furfural can be obtained by the dehydration of the monosaccharides fructose and xylose, respectively, by Brønsted acid catalysis. Templated mesoporous sulfonic carbons (TMSC) have shown outstanding performance as catalysts for these reactions, along with high hydrothermal stability [1]. Therefore, herein, different TMSC were prepared for converting fructose and xylose into HMF and furfural, respectively.

Experimental/Methodology. Carbons of the TMSC were prepared according to the literature: CMK-3 [2], CMK-5 [3], CMK-8 [2], S-CMK-8 [4] and C-Chi [5]. They were pyrolyzed at 550 °C (Carbon-550) or 1000 °C (Carbon-1000) and functionalized, respectively, by sulfonation with fuming sulfuric acid (Carbon-SA) or 4-benzenediazonium sulfonate (Carbon-PSA). All materials were characterized by XRD, N_2 physisorption at 77 K, TGA in O_2, RAMAN, FTIR, XPS, and potentiometric titration. The conversion of the monosaccharides was performed at 130°C for fructose and 160 °C for xylose using THF containing 20 wt. % of water as solvent.

Results and Discussion. XRD confirmed the formation of the expected carbon structures and N_2 physisorption showed that they are mesoporous (3-4 nm) and present high surface areas (700-1900 $m^2\ g^{-1}$). TGA in O_2, RAMAN and C 1s XPS demonstrated that Carbons-1000 present longer defective graphene layers and lower amount of oxidized functional groups than Carbons-550. After functionalization, the catalysts lost the long-range pore organization and had a decrease of their surface areas (450-700 $m^2\ g^{-1}$), although their pore sizes were not affected. In addition, their carbon matrices presented longer defective graphene layers and higher amount of oxidized functional groups. The sulfonic groups were identified by FTIR and S 2p XPS, and a linear correlation between contribution of SO_3H species vs percentage of stronger sites, by potentiometric titration, was found (Figure 1A). The catalytic results showed that the best synthetized catalysts were CMK-3-PSA, CMK-5-PSA, CMK-8-PSA and S-CMK-8-PSA (group CMKs-PSA), achieving HMF and furfural yields close to 65 % and 40 %, respectively. These results were comparable to those of the commercial Amberlysts 15 and 40, however, a correlation between the $TON_{Platform}$ and the percentage of stronger sites was found (Figure 1B), presenting a volcano plot with maximum for the CMKs-PSA catalysts (70-80 % of stronger sites). The $TOF_{Monosaccharide}$ and $TOF_{Platform}$ for these catalysts were determined, and the ratio $TOF_{Platform}/TOF_{Monosaccharide}$ (Figure 1C) showed that CMK-3-PSA is the best catalyst, with ratio of 0.52 for the conversion of fructose into HMF, and 0.27 for the conversion of xylose into furfural.

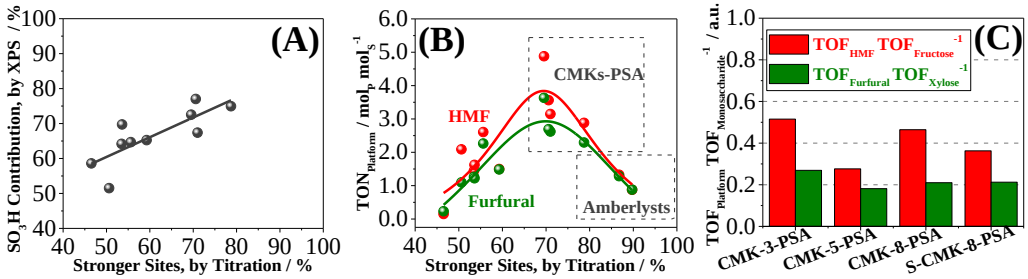

Figure 1. Correlation between stronger sites vs SO_3H contribution of the catalysts synthetized (A). Correlation between stronger sites vs $TON_{Platform}$ of the catalysts synthetized and Amberlysts (B). $TOF_{Platform}/TOF_{Monosaccharide}$ ratio of the CMKs-PSA catalysts (C).

Acknowledgments
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Bio-oil hydrotreatment with novel unsupported catalysts – from model compounds to real bio-oil feeds

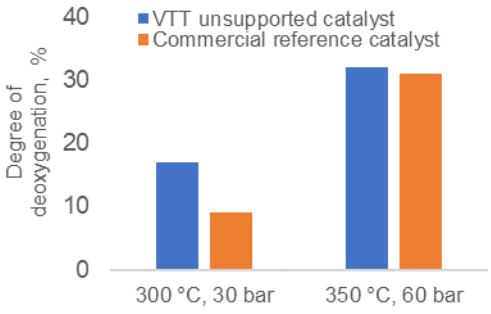
T. Viertiö*, J. Kihlman, N. Vuorio, S. Rautiainen, A. Reznichenko, J. Lehtonen

VTT Technical Research Center of Finland, Espoo, Finland
**tyko.viertio@vtt.fi*

Keywords: biofuels, bio-oil hydrotreatment, hydrodeoxygenation, unsupported catalyst, molybdenum sulfide, slurry hydrotreatment

Introduction. Thermochemically liquefied lignocellulosic biomass, for example fast pyrolysis bio-oil and hydrothermal liquefaction biocrude, are promising feedstocks for sustainable biobased hydrocarbons [1]. However, the high oxygen content, thermal instability and bio-based impurities limit the use of these feeds to heating oil and co-feeding to oil refineries in small quantities, and the lack of technoeconomically viable upgrading routes is the key bottleneck for commercialization of lignocellulosic biomass based hydrocarbon feedstock [1, 2]. Slurry hydrotreatment has been proposed as a potential technology for bio-oil upgrading, enabling addition, removal and circulation of catalyst and unconverted feed during reactor operation and therefore solving the severe bottlenecks of coke formation and catalyst poisoning from thermally unstable and impurity-containing feed [2, 3].

Experimental. Unsupported promoted molybdenum sulfide based catalysts for slurry hydrotreatment of bio-oil were synthetised by hydrothermal precipitation variating synthesis conditions, such as temperature and pH. The catalysts were characterised with XRD, physisorption, XPS, ICP-AES and SEM-EDS, and tested for hydrotreatment of model compound isoeugenol in batch reactor at 300 °C and 30 bar. Furthermore, the catalysts were tested in semi-batch hydrotreatment of fast pyrolysis bio-oil to compare the performance and evaluate the conclusions drawn from model compound experiments. The semi-batch experiments were performed at 300-400 °C and 30-100 bar with continuous hydrogen feed through the reactor to monitor the effect of process conditions to hydrotreatment severity. In addition, catalyst stability was studied by performing catalyst reuse experiments with both, model compounds and bio-oil, and spent catalysts were characterized to monitor potential changes in morphology and composition. Catalyst performance was compared to traditional supported hydrotreatment catalyst as a benchmark.



Results and discussion. Characterization and model compound experiment results show the significant effect of synthesis parameters on the catalyst composition. This work enables tailoring the catalyst for different bio-oil feeds to achieve targeted hydrotreatment performance. In hydrotreatment of real bio-oil feed, unsupported catalysts matched the performance of supported catalyst with comparable loading of active sulfide, as shown in preliminary results in Figure 1. The trends from model compound experiments to real biofeed performance were evaluated.

Figure 1. Comparison of performance of VTT-prepared unsupported catalyst and traditional hydrotreatment catalyst in pyrolysis bio-oil hydrotreatment in semi-batch reactor.

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Valorisation of biomass to phenolics over $Pd/NbOPO_4$ catalyst

R. Jogi[1], A. Samikannu[2], P. Mäki-Arvela[1], J. Hemming[3], A. Smeds[3], C. Mukesh[2], T. A. Lestander[4], C. Xu[3], P. Virtanen[1*], J.-P. Mikkola[1,2]

[1]*Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Henrikinkatu 2, 20500 Turku, Finland*
[2]*Department of Chemistry, Chemical-Biological Centre, Umeå University, SE-90187 Umeå, Sweden*
[3]*Laboratory of Natural Materials Technology, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Henrikinkatu 2, 20500 Turku, Finland*
[4]*Swedish University of Agricultural Sciences, Forest Biomaterials and Technology, SE-90183 Umeå, Sweden*
[*]*pasi.virtanen@abo.fi*

Introduction

Phenolic monomers are mainly derived from fossil resources and have a wide range of applications, *e.g.*, the production of fine chemicals and fuels. One path to diminish the fossil resource dependence leads towards production of bio-aromatics from lignocellulosic biomass. An interesting approach is the catalytic liquefaction technique. It is preliminarily driven by deconstruction or depolymerization of biomass-specific macromolecules (hemicellulose and lignin) into monomers in green solvents (water, methanol, ethanol, propanol, tetraline, etc.) over efficient catalysts, while only crystalline cellulose remains intact [1][2].

Experimental

The wood depolymerisation studies were performed in supercritical ethanol (243 °C) over $Pd/NbOPO_4$ catalyst under hydrogen (initial pressure at RT, 5 bar). 4 g of fresh birch (dry weight, particle size ≤ 250 µm, 32 wt-% moisture content) was first soaked in 90 ml ethanol overnight. Thereafter, the desired amount of $Pd/NbOPO_4$ catalyst (reduced at 400 °C for 3 h and stored in 10 ml ethanol) was added to the reaction medium. The reactor was heated 10 °C/min and stirred slowly during heating. The reaction starting point was taken at the point when the reaction medium reached the desired temperature. The course of the reaction was followed by taking liquid samples from the reactor at different time intervals. The fresh wood, spent solid phases and liquid products were characterised with various analytical techniques such as GC-FID, p-XRD, SEM, TEM, SEC and the catalyst leaching was measured by ICP-OES.

Results and discussion

For the first time, a tandem catalytic material, 5 wt-% $Pd/NbOPO_4$, was utilized in the depolymerization of wood in supercritical ethanol under low initial hydrogen pressure. The results indicated that with fresh birch, 34 wt-% of lignin monomer yield with 84 wt-% delignification efficiency were obtained. The total lignin monomer content extracted from the fresh birch is composed of 77 wt-% of dimethoxyphenols and 17 wt-% with the guaiacol structure. Major lignin monomer product was homosyringaldehyde (62 wt-%). It was concluded that the depolymerization occurred via breaking of the ether bonds in lignin, including ether hydrolysis by Lewis acid sites over the solid acid catalyst and with subsequent deoxygenation of monophenols over Pd. (Fig. 1.)

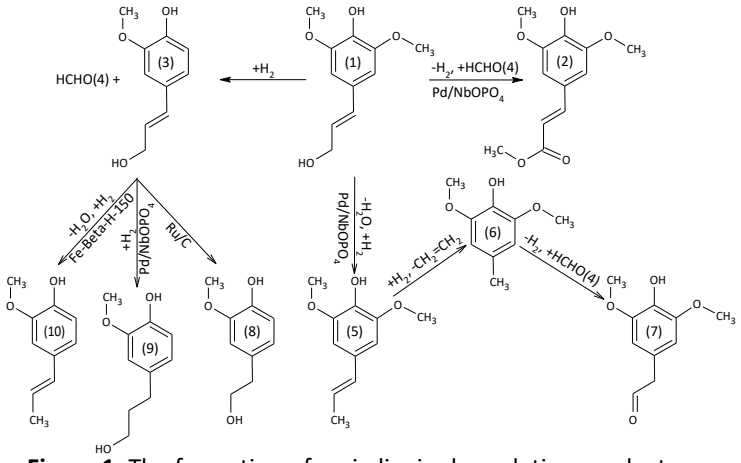

Figure 1. The formation of main lignin degradation products: sinapyl alcohol (1), methyl sinapate (2), coniferyl alcohol (3), formaldehyde (4), 4-propenyl syringol (5), 4-methyl syringol (6), homosyringaldehyde (7), 4-n-propanolguaiacol (8), dihydroconiferyl alcohol (9), and isoeugenol (10)

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Robust Pd/Al_2O_3 bifunctional catalyst for single reactor tandem synthesis of furan and tetrahydrofuran derivatives from furfural

M. Pera-Titus,[1,5*], L. Gao,[1] Z. Jiang,[2] I. Miletto,[3] E. Gianotti,[4] E. Rebmann,[2] L. Baussaron,[2] F. Jiang[1]

[1] *E2P2L, UMI 3464 CNRS-Solvay, Shanghai, China*

[2] *Solvay – Process Innovation Department, Research & Innovation Centre of Lyon, Saint Fons, France*

[3] *Department of Pharmaceutical Sciences, Università del Piemonte Orientale, Novara, Italy.*

[4] *Department for Sustainable Development, Università del Piemonte Orientale, Vercelli, Italy.*

[5] *Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, UK*

PeraTitusM@cardiff.ac.uk

Keywords: Furfural, methyl isobutyl ketone, aldol condensation, single reactor.

Introduction. Furfural (FF) is a valuable building block to access a variety of relevant industrial products and intermediates. Herein we report a robust catalytic system based on a bifunctional Pd/Al_2O_3 catalyst for conducting the single-reactor tandem solvent-free aldol condensation / hydrogenation of FF and methyl isobutyl ketone (MIBK) to access a renewable biosolvent and biofuel precursor in the branched alkane range at high yield. The process comprises two steps (**Figure 1**): (1) aldol condensation/ crotonization, and (2) selective hydrogenation of the aldol condensation adduct. The activity and robustness of the catalyst was investigated in batch and continuous dual fixed-bed reactors to devise conditions for upscaling.

Experimental/methodology. γ-Alumina spheres (Sasol), calcined at 400 °C for 4 h, was used as acid catalyst. Bifunctional Pd/Al_2O_3 was prepared by wet impregnation of palladium acetate on alumina spheres in 30 mL acetone. The sample was dried overnight at 80 °C, calcined at 400 °C for 4 h, and reduced at 200 °C for 4 h under H_2. The single reactor condensation – hydrogenation reaction of FF and MIBK was carried out in: (1) a stainless steel autoclave reactor (30 mL), and (2) dual-type (Al_2O_3-Pd/Al_2O_3) continuous fixed bed reactor. The reaction products were analyzed and quantified by gas chromatography on a Thermo Scientific Trace 1100 GC equipped with a flame ionization detector (FID) and a HP-5 capillary column with 5 wt% phenyl groups (length 30 m; inner diameter 0.25 mm).

Results and discussion. γ-Alumina (spheres) calcined at 400 °C revealed as a robust catalyst for the aldol condensation/crotonization reaction of FF (5.2 wt%) with MIBK, affording quantitative synthesis of (E)-1-(furan-2-yl)-5-methylhex-1-en-3-one at 160 °C for 12 in batch mode with *ca*. 100% carbon balance. The reaction rate decreased at higher FF concentration due to inhibition of Lewis acid centers by adsorbed FF as inferred from kinetic modeling. The spent catalyst could be reused for at least six consecutive catalytic runs without loss of activity due to lack of poisoning of active Lewis acid centers of medium strength as inferred by FT-IR spectroscopy implemented with adsorbed pyridine and NH_3-TPD. With these results, we conceived a single-reactor tandem process over Pd/Al_2O_3 for the aldol condensation of FF and MIBK, followed by hydrogenation with H_2. The system reached an overall 86% yield of 1-(tetrahydrofuran-2-yl)-5-methylhexan-3-one at 180 °C (5.2 wt% FF) after 9 h in batch mode. The catalyst was also operated in a dual-type continuous fixed-bed reactor reaching 55% FF conversion and 60% and 35% selectivity to 1-(furan-2-yl)-5-methylhexan-3-one and (E)-1-(furan-2-yl)-5-methylhex-1-en-3-one, respectively, at 170 °C after 12 h continuous operation at high FF concentration (18 wt%).

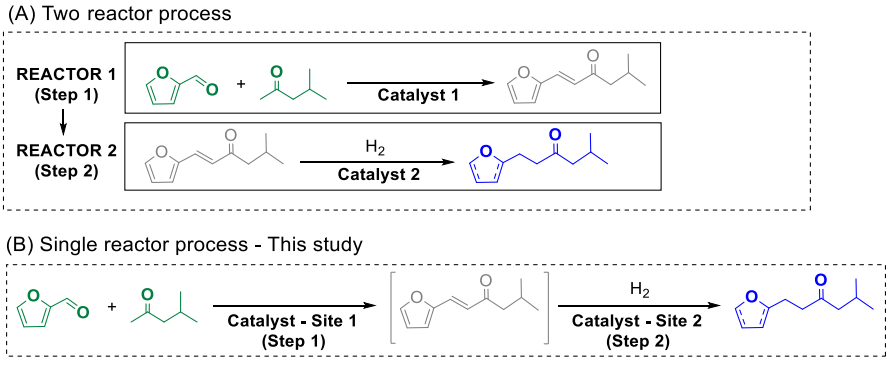

Figure 1. Two-reactor vs. single reactor tandem process for the synthesis of hydrogenated derivatives from FF.

Acknowledgments. *This study was funded by the H2020 programme Multi2hycat (Contract #720783).*

Comparison of K/NaA and K/NaX on transesterification of palm oil

P. Seejandee[1], K. Deekamwong[1,2], N. Osakoo[1,2], S. Prayoonpokarach[1], J. Wittayakun[1*]

[1]*School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, Thailand*
[2]*Institute of Research and Development, Suranaree University of Technology, Nakhon Ratchasima, Thailand*

Keywords: zeolite A, zeolite X, transesterification

Introduction. K/NaX and K/NaY catalysts are active for transesterification of Jatropha seed oil and palm oil [1-4]. Recently, Kosawatthanakun et al. [4] reported that K/NaX is a better catalyst than K/NaY due to its higher basicity and better stability. NaX and NaY have the same structure with a cavity size of 0.74 nm but different Si/Al ratio, namely, 1.2 and 2.4, respectively [4]. In this work, K/NaA is compared with K/NaX. NaA has Si/Al ratio of 1.0, close to NaX, but a cavity size of 0.43 is smaller than NaX.

Experimental/methodology. K/NaA and K/NaX are prepared with a method from [3,4] by impregnation of potassium acetate buffer on commercial zeolites, characterized by XRD, CO_2-TPD, FTIR, and N_2-adsorption-desorption analysis, and tested in transesterification of palm oil with methanol [3,4]. The biodiesel yield was determined by a gas chromatograph coupled with a flame ionization detector.

Results and discussion. The XRD patterns of calcined K/NaA and K/NaX (Figure a,b) indicate that NaA is more stable than NaX under the same preparation procedure. Figure c shows that the basicity of K/NaA (0.68 mmolCO_2/g) is higher than K/NaX (0.37 mmolCO_2/g). Figure d shows that K/NaA gives a higher biodiesel yield than K/NaX. However, both catalysts show deactivations in the second and third cycles.

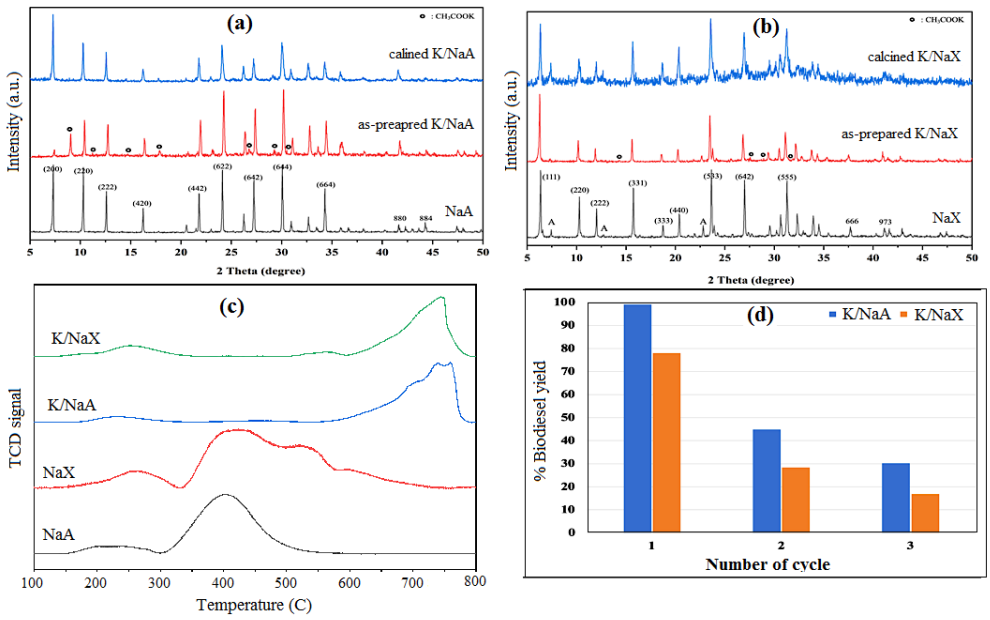

Figure (a) XRD patterns of 12K/NaA, (b) XRD patterns of 12K/NaX, (c) CO_2-TPD profile of calcined catalysts compared with the parent zeolites, and (d) biodiesel yields from 3 cycles at 60 °C for 3 h.

Acknowledgments

The scholarship for P. Seejandee is from Suranaree University of Technology (SUT). K. Deekamwong and N. Osakoo are supported by full-time Doctoral Researcher Grants from SUT.

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Visible-light-driven cleavage of aryl ethers in lignin under mild conditions using non-precious nanocatalysts

Gang Xiao[1,3*], Peifeng Li[1], Yixuan Ouyang[1], Yilin Zhao[1], Sarina Sarina[2], Jan Baeyens[1], Haijia Su[1], Huai-Yong Zhu[2]

[1]*Beijing Key Laboratory of Bioprocess, Beijing University of Chemical Technology, Beijing 100029, P.R. China*

[2]*bSchool of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Brisbane 4001, Australia*

[3]*Current address: Max Planck- Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, U.K.*

[*]*Corresponding to sewicxiao@hotmail.com*

Keywords: Lignin valorisation, aryl ethers, photocatalysis, non-precious nanocatalysts

Introduction. Lignin, a major component of lignocellulosic biomass, is the only large-volume renewable aromatic source in nature. Although currently underutilized, it has a great potential to be valorized to produce aromatic bulk and fine chemicals. The different aromatic subunits in lignin are connected by various types of C-O and C-C linkages. The aryl ether C-O linkages are more abundant and more reactive, and have been considered as the key target to be cleaved for selective and controlled lignin depolymerization. Several efficient thermal-catalysis methods have been developed for the selective cleavage of aryl ether C-O linkages, but harsh conditions and precious metals are always needed.

Results and discussion. Here we developed novel visible-light-driven procedures for this purpose using heterogeneous catalysts of non-precious TiN nanoparticles and ZrO_2 supported Ni nanoparticles. (1) Commercially available TiN nanoparticles were employed to cleave the C-O bond in a β-O-4 dimer model, phenethyl phenyl ether (PPE), with high selectivity to equivalent styrene and phenol under very mild conditions with isopropanol as the green solvent. Direct photon energy input and a free radical mechanism were responsible for this reaction. In addition, the Ti-N-O structure in TiN samples was confirmed to be the active site for cleavage of the C-O bond in PPE in the light reaction.[1,2] (2) Using non-plasmonic Ni nanoparticles, three aryl ether bonds in lignin were successfully cleaved under mild conditions with excellent conversion and good to excellent selectivity under visible light irradiation. We used solar irradiation to demonstrate a significant reduction in the total energy consumption. The light irradiation excited interband transitions in Ni nanoparticles and the resultant energetic electrons enhanced the activity of reductive cleavage of the aryl ethers. Its application potential was illustrated by the depolymerization of dealkaline lignin to give a total monomer yield of 9.84 wt% with vanillin, guaiacol, and apocynin as the three major products.[3]

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Synthesis of Jet-Fuels from Renewable Biomass through Aldol Condensation of Cyclopentanone and Furfural on Different Base Catalysts

Olha Yevdokimova[1]*, Natalia Shcherban[1], Mark Martinez-Klimov[1], Irina L. Simakova[1,2], Päivi Mäki-Arvela[1], Kari Eränen[1], Dmitry Yu. Murzin[1]

[1]*Åbo Akademi University, Turku/Åbo, Finland*
[2]*Boreskov Institute of Catalysis, Novosibirsk, Russia*
[*]*olha.yevdokimova@abo.fi*

Keywords: jet fuel, renewable sources, catalyst, MOFs, aldol condensation

Introduction.

There has been a substantial interest in conversion of biomass to materials, chemicals and fuels. Several strategies for production of renewable jet fuel with a much lower environmental footprint than fuels currently in use have been explored [1]. One of such options is aldol condensation of furfural with biomass derived ketones, e.g. cyclopentanone – Figure 1, followed by subsequent hydrodeoxygenation [2]. There is a very limited number of studies on heterogeneous catalytic aldol condensation, which prompted a detailed investigation of furfural aldol condensation with cyclopentanone using a range of catalysts with base properties

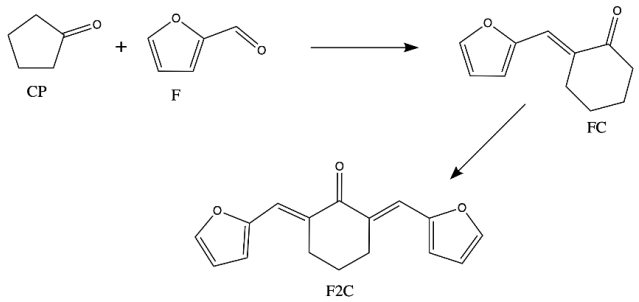

Fig. 1. Reaction scheme for the aldol condensation of cyclopentanone and furfural.

Experimental/methodology.

In this work, the aldol condensation of cyclopentanone and furfural was investigated at 40 – 60 °C, in the presence or absence of a solvent (alcohols, water and their mixtures) in a glass reactor equipped with magnetic stirring under N_2 atmosphere. As a catalyst, materials with different porosity and basicity were selected, namely: hydrotalcites, CaO, NaOH, $NaAlO_2$ and a range of MOFs of UiO-66 structure, Cs-forms of hierarchical zeolites, basic metal oxides deposited onto hierarchical zeolites, etc.

Samples were analysed by gas-chromatography and gas-chromatography coupled to a mass-spectrometer. Fresh and spent catalysts were characterized by a range of physico-chemical methods such as SEM-EDX, TEM, ICP-OES, TPR, CO_2-TPD, TGA, N_2-physisorption and soluble coke extraction analysed by GC-MS. The products were separated from the catalyst and reagents by dilution with ethyl acetate and further filtration. The chemical structure of products was confirmed by gas chromatography with a mass detector and FID, as well as by NMR.

Results and discussion.

Basicity of the catalysts was determining activity, while the ratio between the condensation products (FC to F_2C) was seen to be dependent on the excess of the ketone as well as on the type of solvent and the fraction of alcohol. More details on the catalyst preparation, characterization and catalytic tests will be given in the final presentation.

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Alcohol dehydration on Lewis and Brønsted acid sites of tungsten-oxide based catalysts

Florian Zahn[1], Niklas Pfriem[1], Johannes A. Lercher[1*]

[1] *Department of Chemistry and Catalysis Research Center, TU München, Garching, Germany*
[*] *johannes.lercher@tum.de*

Keywords: alcohol dehydration, tungstated materials, support effects

Introduction

Supported metal oxides have been widely used for acid-catalyzed reactions in recent centuries due to their thermal stability and acid strength. Tungsten oxide-based solid acids have been previously employed as suitable catalysts in gas-phase isomerization reactions, alcohol dehydration, and liquid-phase upgrading processes of biomass-derived feedstocks [1-2]. Until now, the literature lacks an understanding of the mechanisms of alcohol dehydration over tungsten oxide-based Lewis acids and how the nature of the LAS impacts alcohol dehydration [3]. In this work, we doped tungsten oxide on zirconia (WO_x/ZrO_2) and γ-alumina (WO_x/Al_2O_3) to achieve a stable and active catalyst domain consisting of both BAS and LAS to invest the influence of LAS on the dehydration of cyclohexanol. To distinguish between LAS- and BAS-catalyzed dehydration, we perform in-situ titration experiments and use IR experiments.

Experimental/methodology

A series of WO_x/support (ZrO_2, γ-Al_2O_3) catalysts were synthesized *via* incipient wetness impregnation of $Zr(OH)_4$/ γ-Al_2O_3 with aqueous solutions of ammonium metatungstate hydrate containing desired amounts of tungsten. The dried samples were calcined in flowing synthetic air at 973 K for four hours and then cooled to room temperature. The catalysts were characterized by AAS, BET, PXRD, Raman spectroscopy, and IR spectroscopy of adsorbed pyridine. Dehydration of cyclohexanol was carried out in a 300 ml Hastelloy Parr reactor. In a typical experiment, 100 mL of a 0.05 – 1.0 M cyclohexanol solution (solvent: decalin) and ~100 mg of catalyst were added to the reactor. The distinction between acid sites, i.e. Brønsted acid sites (BAS) and Lewis acid sites (LAS), was achieved by titration experiments with pyridine, 2,6-di-tert-butylpyridine (DTBP), and piperidine under reaction conditions.

Results and discussion

For all tested catalysts, the dehydration rates decreased linearly with increasing titrant uptake for all three organic base titrants, irrespective of the catalyst. However, complete suppression of the dehydration rate was not achieved by either pyridine or DTBP. Fully suppression occurs only with piperidine for the -alumina supported catalyst. Overall, we have on WO_x/ZrO_2 catalysts at least three classes of sites: (1) active sites that bind all three titrants and contribute most to the catalytic activity; (2) weak acid sites that do not bind pyridine/DTBP but bind piperidine and are inactive for dehydration; (3) weak acid sites that bind none of the N-titrants but are catalytically active. The inactive acid sites and the sites responsible for the remaining dehydration rates may be weak BAS or LAS. Their exact chemical identity cannot be determined from these experiments and will be further discussed with IR experiments.

Significance

We provide an understanding of LAS-catalyzed dehydration routes for heterogeneous tungstate catalysts, using cyclohexanol as an alcohol representative for a class of molecules derived from biomass upgrading reactions. This work is expected to lead to improved metal-oxide catalyst design for biomass upgrading reactions.

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In-depth study of reductive catalytic fractionation of biomass towards highly functional lignin oligomers as bio-based polymer substrates

Yingtuan Zhang[1] and Bert F. Sels[1*]

[1]*Center for Sustainable Catalysis and Engineering, Faculty of Bioscience Engineering, KU Leuven, Heverlee 3001, Belgium.*

**bert.sels@kuleuven.be*

Keywords: lignin, reductive catalytic fractionation(RCF), bio-based, polymer

Introduction. As the most abundant natural source of renewable aromatic molecules on earth[1], lignin, particularly lignin oligomers, has been considered a promising substrate for bio-based polymers[2]. In the recently developed reductive catalytic fractionation(RCF) of biomass under the 'lignin-first' biorefinery concept, a considerable amount of phenolic lignin oligomers is generated[3]. However, an in-depth study of the RCF process targeting highly functional lignin oligomers as bio-based polymer substrates is still absent. Here, we report a systematic study of the RCF process towards highly functional lignin oligomers as bio-based polymer substrates.

Experimental/methodology. Lignocellulosic substrates including birch, pine and flax shives were studied as being a syringyl-unit-rich hardwood, a guaiacyl-unit-rich softwood and an unvalorized industrial byproduct. Similarly, catalysts including Pd, Ru, and Ni and solvents including methanol, ethylene glycol and a 50:50 butanol-water solution were investigated to discover the optimized solvent-catalyst system. To monitor the product, the molecular weight distribution of the produced lignin oligomers was characterized by gel permeation chromatography, while the OH content was determined by P-NMR.

Results and discussion. Starting from a conventional Ru-Methanol system, and ending in some new combination such as the Ni-Ethylene glycol system, it was discovered that different catalyst-solvent systems had significant effects on the lignin oligomers' structure—molecular weight and hydroxyl groups content. Besides, the changes in hydrogen pressure, temperature and time had a direct effect on the reaction's severeness, which consequently influenced mainly the lignin oligomer's yield as shown in Figure 1.

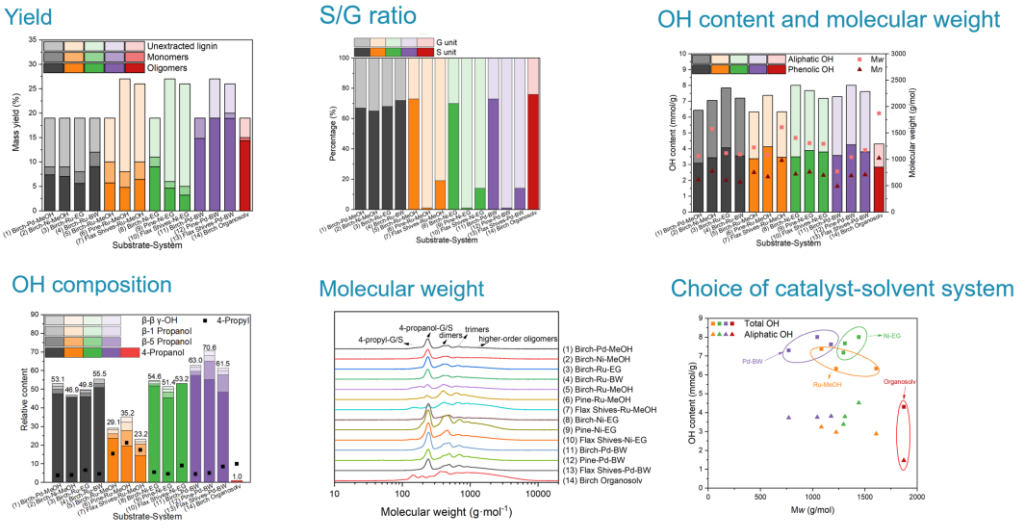

Figure 1. The influence of various RCF parameters on the properties of lignin oligomers.

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Conversion of lactic acid to acrylic acid over Ba-modified SBA-15

Rong Zhao[1], Jong Wook Bae[1*]

[1]*School of Chemical Engineering, Sungkyunkwan University(SKKU), 2066 Seobu-ro, Jangan-gu, Suwon, Gyeonggi-do,16419, Republic of KoreaCountry*

[*]*Corresponding Author (J.W. Bae) address: finejw@skku.edu*

Keywords: biomass, dehydration, lactic acid, acrylic acid, barium, catalyst

Introduction. Acrylic acid has been used to produce adhesives, textiles, dispersants, thickeners, and so on [**1,2**]. The selective catalytic oxidation of propylene or propane from non-renewable chemicals was responsible for a significant pollution, expensive investment and several issues to be resolved. Catalytic conversion of lactic acid to acrylic acid (LTA) on heterogeneous catalysts with appropriate acidity and basicity has been attracted due to lactic acid can be obtained cheaply through the fermentation of various biomass resources [**3**]. It is unavoidable that the LTA reaction can be followed by competitive reactions according to the strong reactivity of its hydroxyl and carboxyl groups. This research revealed the effective conversion of lactic acid into acrylic acid by utilizing efficient catalyst (high conversion and selectivity on the Ba-incorporated SBA-15) in a fixed bed reactor.

Experimental/methodology. The preparation of the catalysts is as follows: Firstly, the ordered mesoporous silicon-based SBA-15 support was prepared by using a P123 template, and the precursor materials Ba $(OH)_2 \cdot 8H_2O$ were dissolved in a certain amount of deionized water. And then impregnated the precursor on the SBA-15 support by using the dry impregnation method. Finally, the catalysts obtained after drying and calcination were recorded as Ba (x)/SBA-15, where x represents the content ratio of Ba metal. The activity test was carried out on a fixed-layer reactor. First, the catalyst was loaded into the middle of the reactor in the form of a sandwich (wrapped with quartz wool), and then 30wt% of the lactic acid aqueous solution was pumped into the reactor. After the pretreatment at 200 °C for 2h under a flow of N_2 gas, the reactor was heated to 350 °C and the sample collected every 1 h and analysze with FID- equipped GC.

Results and discussion. All the catalysts synthesized showed highly ordered mesoporous structures, and the SBA-15 support itself showed a poor LTA activity (LA conversion of 23.0%, and AA selectivity of 11.93%). With an increase of Ba content, the conversion and selectivity of LA were continuously increased and the conversion of lactic acid was increased up to 94.7% with AA selectivity of 87.6% on the Ba(17)/SBA-15. However, with the further increase of Ba contents, the accumulated Ba oxides seem to block the active sites, resulting in showing a lower AA selectivity as shown in **Figure 1**. The excellent activity of the Ba (17)/SBA-15 was mainly attributed to the appropriate surface acidic and basic sites as shownin **Figure 1**.

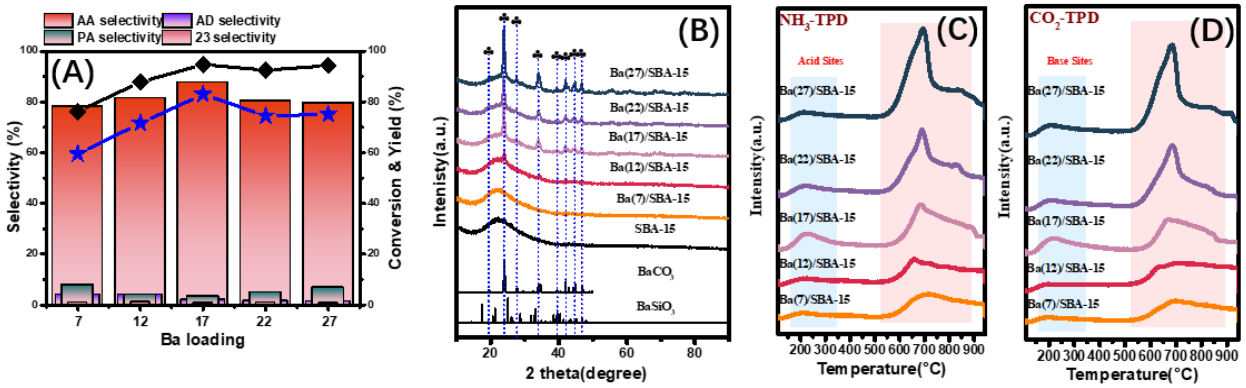

Figure 1. (A) LTA activity, (B) XRD patterns, (C) NH_3-TPD patterns on the fresh Ba(X)/SBA-15, and (D) CO_2-TPD patterns on the fresh Ba(X)/SBA-15 catalysts.

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Effect of the hydroxyapatite modification with alkaline earth elements and of the nature of the carbon support on its catalytic activity in Guerbet condensation of butan-1-ol

O.V. Zikrata[1*], O.V. Larina[1], N.D. Shcherban[1], I. Khalakhan[2], K. Veltruská[2], G. Mali[3], S.O. Soloviev[1]

[1] *L.V. Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine*
[2] *Charles University, Prague, Czech Republic*
[3] *National Institute of Chemistry, Ljubljana, Slovenia*
[*] *oksanazikrata@ukr.net*

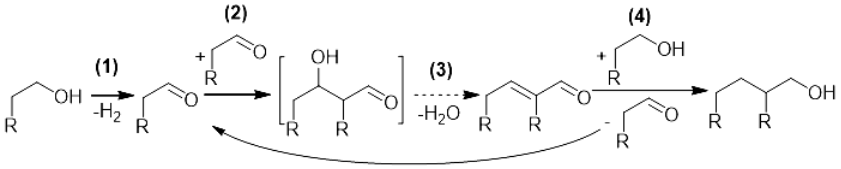
Keywords: Butan-1-ol conversion; Guerbet reaction; Carbon support; Hydroxyapatite.

Introduction. Alcohols obtained by fermentation of renewable non-food biomass are promising source of raw materials for obtaining industrially important compounds, including unsaturated hydrocarbons and oxygenates. Butan-1-ol (BuOH) can be received by the ABE process and Guerbet condensation of bio-ethanol (EtOH-to-BuOH). BuOH can be used as a precursor for the synthesis of 2-ethylhexan-1-ol (required for the production of solvents, plasticizers, soaps, diesel additives etc.) by BuOH condensation (BuOH-to-2-EH) over alkali cation zeolites, metal oxide systems and hydroxyapatites, $Ca_{10}(PO_4)_6(OH)_6$ (HAP). The last are highly selective catalysts towards the target BuOH in the EtOH-to-BuOH process [1].

This work highlights several approaches to obtain an active and highly selective catalyst for the BuOH-to-2-EH process. The first consists of the modification of Ca-containing HAP structure by partial replacement of Ca^{2+} with Mg^{2+} and Sr^{2+} [2]. The second involves the deposition of Ca-containing HAP on various types of carbonaceous materials (CM) [3].

Experimental/methodology. The HAP catalysts were synthesized by the method described elsewhere [2]. The preparation of carbon-supported HAP samples was performed by wet mixing the components, namely HAP and various carbonaceous materials. Physical-chemical characteristics of the catalysts were studied by XRD, FE-SEM with EDX, N_2-ad/desorption, ^1H and ^{31}P MAS NMR, Raman spectroscopy, XPS, EPR, TPD-NH_3/CO_2. The catalytic activity tests of the prepared samples were performed in a fixed-bed flow quartz reactor under atmospheric pressure.

Results and discussion. It was found that the partial replacement of calcium in the HAP structure by 2.5 % mol. magnesium leads to redistribution of the number and strength of basic and acidic surface sites necessary for the BuOH dehydrogenation and aldol-crotonic condensation, respectively (Scheme). Such balance between the surface-active sites allows to achieve the high selectivity towards 2-EH (77.5 % at 573 K) in the BuOH-to-2-EH process. In the case of the BuOH conversion over carbon-supported HAP catalysts, the alcohol conversion and selectivity towards target product are highly dependent on the nature of the carbonaceous materials. The highest yield of 2-EH (up to 21%) is achieved on HAP/activated coconut charcoal. HAP modification by magnesium also leads to increasing the catalyst resistance to deactivation with time-on-stream, which opens up prospects for using of hydroxyapatites in the BuOH-to-2-EH process.



Scheme. Guerbet reaction mechanism: 1 - initial alcohol dehydrogenation to aldehyde, 2 - aldol condensation, 3 - crotonic condensation, 4 - hydrogenation and/or reduction of unsaturated aldehyde.

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The kinetics of fatty acid hydrodeoxygenation

M. Žula[1*], M. Grilc[1], B. Likozar[1]

[1] *Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia*

Keywords: Hydrodeoxygenation, sulfided NiMo,fatty acids, reaction kinetics

Introduction. Fatty acids and triglycerides are one of the most promising medium term renewable sources for the preparation of fuels and chemicals. Their similarity to the crude oil promises broad application with minimal adaptation of existing systems. Thus, the commercial application would enter an already established huge market of fuels and chemicals. The sources for triglycerides are broad and range from microalgae oil to waste cooking oil, all of which can be catalytically converted to fuels and chemicals [1]. To understand mechanisms and describe its kinetics a mathematical model was written.

Experimental. The experiments were conducted in a 75 mL Parr batch reactors in a temperature range between 225 and 275 °C in a hydrogen atmosphere at pressures between 30 and 70 bar. In a typical experiment 1 g of palmitic acid reacted with 0.1-0.4 g of sulfided NiMo catalyst. To expand the understanding of the mechanisms, the intermediates – in the form of fatty alcohol, ester in the hydrogen and nitrogen atmosphere were also modeled. The catalyst parameters in the form of surface area, metal loading, pore size and volume, XRD, SEM, TEM and NH_3-TPD were reported. Additionally, the quantum calculations were performed using GPAW ASE software.

Results and discussion. The resulting model differs from the convential Langmuir-Hinshelwood models [2] by the separation of the liquid and solid phase with the longterm goal of including a solid phase descriptions and data in kinetic models. We show that for such model to be able to describe the kinetics of the process the adsorption selecitvity is highly relevant. As some models have previously shown the alcohols will be barely reactive while the fatty acid is present while aldehydes and alkenes will be present in relatively low quantities in liquid phase. The concentration of the solvent and the product will not impact the kinetics due to very low adsorption energy. Thus, in the model the products were unable to adsorb on the catalyst surface, while the alcohols had a lower adsorption rate than other presents species which was determined experimentaly using fatty alcohol feedstock alone and in combination with the fatty acid. To confirm the findings theoretically, the adsorption energies for the long-chain species were calculated and have shown that the model findings are indeed correct. The model and experimental results for pressure variation are presented in Figure 1.

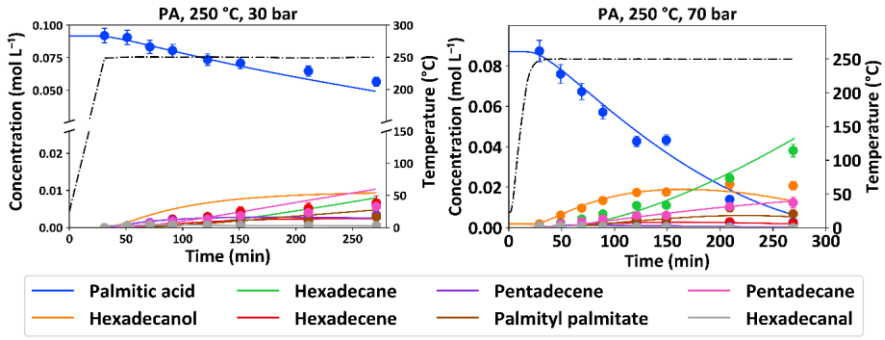

Figure 1: The model results for the variation of hydrogen pressure.

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Oxidative cleavage of UFAs in Palm oil with Ru carbon catalyst

Author's Name (Calibri, 12 pt.) e.g. S. Gámez[1*], E. de la Torre[2], E. M. Gaigneaix[1]

[1] *Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Place Pasteur 1, L4.01.09, 1348 Louvain-la-Neuve, Belgium*

[2] *Department of Extractive Metallurgy, Escuela Politécnica Nacional, Ladron de Guevera E11-253, Quito 170517, Ecuador*

[*] *sebastian.gamez@uclouvain.be*

Keywords: oxidative cleavage, polydopamine, ruthenium, palm oil

Introduction. Oxidative cleavage (OC) involves the rupture of carbon-carbon double bonds in alkenes for the production of carbonyl compounds of high added value.[1] Most of the works related to this matter are focused on small and aromatic alkenes, but only few of them address unsaturated fatty acids (UFAs).[1,2] Yet UFAs can be cleaved into dicarboxylic acids, eventually with an odd number of carbon atoms rare in nature and highly demanded for polymer and pharmaceutic applications. This is typically the case of azelaic acid accessible by OC of oleic and linoleic acids, making these reactions particularly interesting.[2] To date, OC of UFAs is mainly performed using homogenous catalysts which are pollutant and cannot be recovered. On the other hand, current heterogeneous catalysts display poor activity due to the poor contact amid the UFA and the active phase.[1-3] To solve this issue, we demonstrate the efficiency of a Ru (namely a very active element in OC of UFAs),[3] catalyst supported on carbon black functionalized with polydopamine (PDA). The latter is a natural polymer containing catechol and amine groups available to chelate Ru for the oxidative cleavage of UFAs inside Palm oil.

Experimental/methodology. Precisely, oxidized carbon black (CBO) was put in contact with an aqueous dopamine solution under basic conditions in order to trigger the self-polymerization process over the support. The support plus the deposited polymer (CBO-PDA) was recovered by centrifugation and dried at room temperature overnight. Ru was deposited on CBO-PDA surface by wet impregnation using a $RuCl_3$ aqueous solution to achieve a 2 wt% load. OC tests were carried out with Ecuadorian palm oil using 100 mg of CBO-PDA-Ru catalyst along with $NaIO_4$ as oxidizing agent at room temperature for 24 hours under agitation and air atmosphere.

Results and discussion. Figure 1 displays FTIR spectra with the characteristic bands of the polymer on CBO surface while N_2 physisorption isotherms confirm a decrease in surface area after PDA deposition on macroporous CBO. Ru 3p core level appears as a doublet at 463.5 and 485.7 eV attributed to Ru(III)-catechol species as a result of Ru interactions with PDA functional groups. The catalyst with $NaIO_4$ was assessed in the OC of oleic and linoleic acids inside palm oil maintaining its catalytic activity up to 5 recycles for azelaic acid production (Yield ~95%). This new catalyst opens a novel route to the production of a high value-added product with medicinal applications from a cheap feedstock as palm oil.

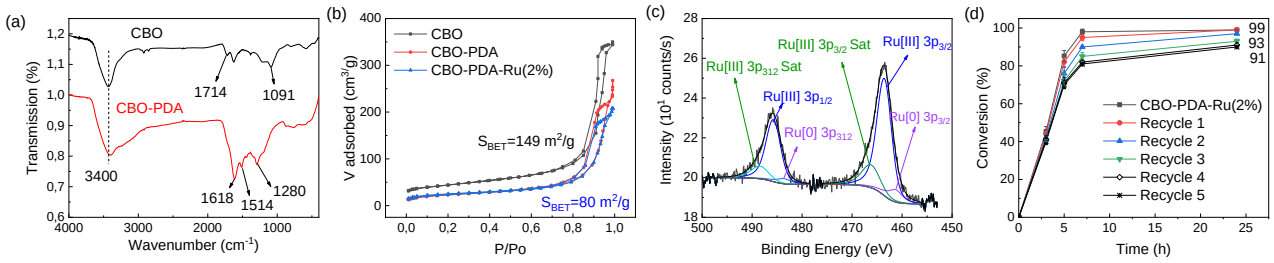

Figure 1. a) FTIR spectra; b) N2 physisorption isotherms; c) XPS Ru 3p; d) Recycling tests

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Selective one-step hydrotreatment of methyl palmitate over Co- and Mo-supported beta zeolite

S. U. Lee, T. W. Kim, K. E. Jeong, S. Y. Jeong, C. U. Kim*

Chemical & Process Technology Division, Korea Research Institute of Chemical Technology, Yuseong, Daejeon, 34114, South Korea
**cukim@krict.re.kr*

Introduction. For producing a drop-in bio jet fuel, one-step hydrotreatment, which includes deoxygenation, isomerization and cracking in one step, is essential to overcome the typical biofuel drawbacks due to high oxygen content, out of jet fuel range hydrocarbons, and low isomerization degree. In this study, Co-or/and Mo-supported Beta(25) zeolites with various Co/Mo ratios were prepared as transition metal-supported zeolite catalysts for selective one-step hydrotreatment to produce bio jet fuel range hydrocarbons.[1]

Experimental/methodology.

1. Synthesis of catalysts: Co- or/and Mo-supported Beta(25) zeolites were prepared by wet-impregnation method, and denoted as "Co_xMo_y/Beta(25)", where 'x' and 'y' are the weight % of Co and Mo.
2. Catalytic performance tests of methyl palmitate as a biofuel model component of fatty acid methyl esters were carried out in a semi-batch reaction system (280 °C, 20 bar, 2 h).

Results and discussion. With controlling the Co/Mo ratios, Co_xMo_y/Beta(25) comprises not only Co_3O_4 and MoO_3, but also $CoMoO_4$ due to the preference for the formation of $CoMoO_4$ (Table1). Regrarding Co metal phase, Co_2Mo_{10}/Beta(25) and Co_3Mo_{10}/Beta(25) consist of $CoMoO_4$, and start to concurrently appear Co_3O_4 from Co_5Mo_{10}/Beta(25). Importantly, the Co metal phase strongly influences the acidic properties of Beta(25) by the formation of Lewis (L) acid sites with different strengths as Co_3O_4 and $CoMoO_4$ for strong and weak L acid sites, respectively (Table 1). In hydrotreatment of methyl palmitate (Figure 1), deoxygenation of methyl palmitate is preceded by Co with the aid of strong L acid sites. Among Co_xMo_y/Beta(25), Mo plays the role to suppress cracking and increase the selectivity for light alkanes, and Beta(25) can enhance isomerization with hydrogenation promoted by Co. From the results, Co_5Mo_{10}/Beta(25) zeolites achieved the highest C_8–C_{16} selectivity of 89.7 wt% including isomer ratio of 83.8% in organic liquid product with the conversion of 94.2%.

Table 1. Acidic properties of groups by metal phases.

Group	Sample	Metal phase	NH_3-TPD	FTIR of adsorbed pyridine		
			Acid sites (mmol/g)	B* (mmol/g)	L* (mmol/g)	B/L*
I	Co_{10}/Beta(25)	Co_3O_4	1.33	0.17	1.16	0.15
II	$Co_{10}Mo_5$/Beta(25)	Co_3O_4 + $CoMoO_4$	1.37	0.19	1.18	0.16
	$Co_{10}Mo_{10}$/Beta(25)		1.20	0.18	1.02	0.18
	Co_5Mo_{10}/Beta(25)		1.37	0.20	1.17	0.17
III	Co_3Mo_{10}/Beta(25)	$CoMoO_4$ + MoO_3	1.14	0.21	0.93	0.23
	Co_2Mo_{10}/Beta(25)		1.20	0.31	0.89	0.35
IV	Mo_{10}/Beta(25)	MoO_3	1.19	0.78	0.41	1.89
	Beta(25)	-	1.24	0.58	0.66	0.88

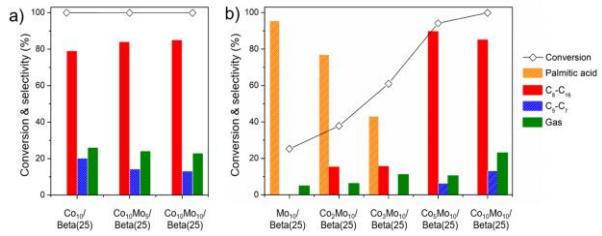

Figure 1. Catalytic activities of metal palmitate

Acknowledgments

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Impact of catalytic hydrotreatment over simulated pyrolysis oil for bio-char formation

Elham Nejadmoghadam[1], Abdenour Achour[1], Olov Öhrman[2], Prakhar Arora[2], Louise Olsson[1], Derek Creaser[1*]

[1]*Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden*
[2]*Preem AB, Gothenburg, Sweden*
[*]*derek.creaser@chalmers.se*

Introduction. Pyrolysis oil obtained from biomass has inferior properties such as low energy density due to high oxygen and water content, high acidity, and immiscibility with petroleum-derived fuels, which limit its utilization. Therefore, catalytic upgrading is essential to apply it as a high-quality fuel. A two-stage hydrotreatment is therefore beneficial in which pyrolysis oil is first stabilized at a lower temperature (150−300°C) before it is heated to a high temperature (350−400°C) where the majority of the oxygen removal takes place [1]. In this study, we aim to minimize and understand the nature of solids formed at the mild conditions over various ɣ-alumina supported catalysts.

Experimental/methodology. Monometallic (Pd, Pt, Rh, Re), 2 wt. % and bimetallic (NiMo), 5 wt.% Ni and 15 wt.% Mo catalysts supported on pre-calcined ɣ-alumina were prepared. Acetic acid, hydroxyacetone, benzaldehyde, guaiacol, 5-hydroxymethylfurfural (HMF), and levoglucosan were selected to represent acids, ketones, aldehydes, phenols, furans, and sugars respectively in real pyrolysis oil. This simulated pyrolysis oil in hexadecane was heated to 180°C , with 60 bar of H_2. Thereafter the reaction was continued for 4h at 180°C. After collecting the liquid product, the catalyst and solid residue in the reactor were removed with acetone and dried. Soluble and insoluble (char) extractions of the total solid product were separated through DMSO rinsing. The soluble fraction contains more oxygenates while the insoluble fraction is largely carbonaceous compounds.

Results and discussion. Various catalysts present different behaviors in mild hydrotreatment of simulated pyrolysis oil. The solid yields obtained from mild hydrotreatment are given in Figure 1(a). Among these catalysts, Pd/Al_2O_3 was the most active catalyst in mild hydrotreatment of simulated pyrolysis oil to produce minimum solid/char yields. The presence of Pd/Al_2O_3 and Rh/Al_2O_3 catalysts causes a large portion of the solid product to be DMSO soluble while it was the opposite for the other catalysts. The results also show NiMo catalyst performs much better compared with Re and Pt in terms of suppressing the solid formation. We also found a correlation between the color of liquid products and the yield of solids. This evidence indicates the higher yield of solids is accompanied by the darker yellow coloration of the liquid sample which suggests that the DMSO soluble fraction is humin formed during the mild hydrotreatment of levoglucosan and HMF [2], [3]. Different loadings of Pd over Al_2O_3 (2 to 5 wt%) were also investigated (see Figure 1b). Higher amounts of total solids were found by increasing the catalyst metallic loadings from 2 to 5wt%. However, they were mostly composed of the soluble fraction for 5 wt% Pd/Al_2O_3.

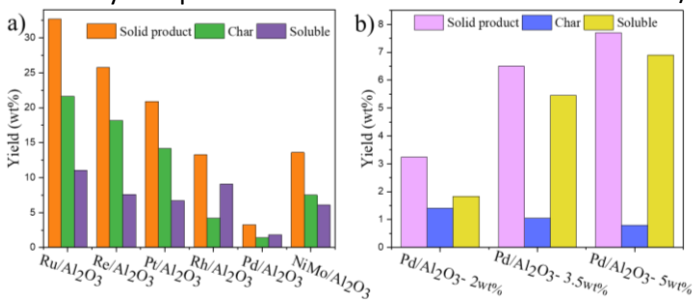

Figure 1. The yield of total solid, char and soluble fractions from stabilization of simulated pyrolysis oil (180°C, 60 bar of H_2, 4 h). a) in presence of different catalysts. b) in presence of Pd/Al_2O_3 catalysts with loading 2-5 wt%.

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CO2 valorization

Ni- based catalysts for CO_2 methanation: effect of promoters and development of intermetallics based materials

P. Riani[1,2], E. Spennati[2,3], R. Freccero[1,2], G. Garbarino[2,3*]

[1]*DCCI University of Genova, Genova, Italy*
[2] INSTM, UdR Genova, Genova Italy
[3]*DICCA University of Genova, Genova, Italy*
[*]*gabriella.garbarino@unige.it*

Keywords: CO_2 hydrogenation, Ni catalysts, Intermetallics, Power to Methane, Carbon capture and utilization

Introduction. In the frame of green-houses gas reduction, the development of CO_2 capture and utilization technologies is recognized as a key-target to achieve carbon neutral economy by 2050 and attracted the attention of catalysis community in the optic to reduce emissions arising by the energy sector and develop circular economy approaches. In literature, Ru and Ni are recognised as active phases [1], and the addition of suitable promoters manganese [2], lanthanum [3,4] and cerium [5] among others have been investigated; however, their optimum loading might be different as a function of the support and preparation procedure, thus being still matter of debate, and moreover a comparison with suitable intermetallics seems to be fruitful.

Experimental/methodology. A series of catalytic materials have been prepared by classical and novel synthetic routes i.e., sequential incipient wetness impregnation, co-impregnation, etc, by keeping a constant Ni loading of 13.6 wt.%, found as optimum from previous studies. Promoters loading have been varied in the range 0-37 wt.%. In parallel, aluminium/nickel, lanthanum/nickel, and cerium/nickel intermetallic compounds have been prepared weighing the metals in the proper stoichiometric ratio. The samples were prepared using an arc melting unit under argon atmosphere. Both fresh and exhaust catalysts have been fully characterized by BET, XRD, FE-SEM, IR, UV-vis-NIR. The assessment of catalytic performances has been carried out at atmospheric pressure and by both increasing and decreasing the reaction temperature in the range 523-773 K in diluted conditions and by keeping a GHSV of 55000 h^{-1}. Evaluation of catalytic performance in on-demand application has been also assessed.

Results and discussion. Supported catalytic materials have been found performant in the investigated reaction, by achieving remarkable conversion and methane selectivities at low temperature and, approaching thermodynamic equilibrium at higher temperatures i.e., above 673 K. Interesting results have been also obtained for intermetallic derived catalysts, allowing the understanding of such novel application of these materials. In the case of La- supported Ni/Al_2O_3 catalysts, results confirmed a quite remarkable effect of the followed preparation procedure. In the present work, Ce-based catalysts resulted more active than La-based ones and best methane yield is 92% at 623 K.

Acknowledgments

GG acknowledges University of Genova for fundings. PR acknowledges INSTM for funding in the project INSTM22GE1.

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Activity of Ni modified WO_3 doped CeO_2-ZrO_2 based catalysts in selective methanation of CO_2: effect of Ce/Zr ratio and WO_3 loading

P.K. Seelam[1,2*], P. Balla[3], S. Kim[3], U. Lassi[2]

[1]*Sustainable Chemistry Research Unit, Faculty of Technology, P.O. Box 4300, University of Oulu, Oulu-90014, Finland.*

[2]*Hycamite TCD Technologies Oy, Kemirantie 15, Kokkola-67900, Finland.*

[3]*Department of Chemical Engineering and Applied Chemistry, Chungnam National University, Daejeon-34134, Republic of Korea.*

Keywords: Ceria-zirconia; Ni; CO_2; SNG; PtG

Introduction

Utilizing CO_2 in power-to-gas (P2G) is a novel concept in low carbon gas technologies. EU aim is to net zero carbon emissions by 2050 to achieve low to zero Carbon Society [1]. Two approaches exist to the current problem, either the use of non-carbon energy and fuel technologies or to convert the abundant CO_2 gas to valuable compounds. The former one is the long-term solution and the later can be a present solution. If the net gained CO_2 can be effectively utilized to make synthetic fuels, it can significantly reduce carbon emissions. Producing synthetic natural gas (SNG) *i.e.* mainly CH_4 from CO_2, which is also called as methanation, is of great interest in the scientific and industrial community [2].

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O,\ \Delta H^0_{298K} = -206\ kJ\ mol^{-1}$$

Experimental/methodology

First, CeO_2-ZrO_2 supports were prepared with molar compositions ceria and zirconia precursors by co-precipitation method. In the next step, sequential wet impregnation was done by using dopant tungstate salt (WO_3) & Ni 10 wt.% loadings. The catalysts was characterised by XRD, TEM, TPR, TPD, ICP, etc. The activities of the catalysts were tested in CO_2 methanation. The methanation reaction was performed in a quartz fixed bed reactor uder atmospheric pressure. Typically, in each experiment, catalyst powder was packed in the reactor which was fixed vertically inside a furnace and a thermocouple was embedded in the middle of catalyst bed to measure the reaction temperature. The catalyst was then reduced under 15%H_2/N_2 flow of 85 mL.min^{-1}for 30 min at 400°C. The gaseous reactant mixture *i.e.* CO_2:H_2:N_2 (1:4:16) was fed to the reactor with N_2 and total volumetric flow rate of 800 mL.min^{-1}.

Results and discussion

In this work CO_2 methanation is studied over Ni modified WO_3 doped CeO_2-ZrO_2 mixed oxides catalysts with different Ce/Zr molar ratios and the WO_3 loadings (1-6 wt.%). As predicted effect of temperature had profound influence and compared the results with the equilibrium conversion. The nature of the support and the composition determine the metal-support interactions and its role in enhanced activity. Overall, the catalyst with optimized CeO_2-ZrO_2 50 wt.% and addition of 6 wt.% WO_3 was found to be the most desirable composition in gaining highest activity. The degree of Ni dispersion and the optimal strength of basicity and the reducibility varied with the support composition. The catalyst was stable during the time of stream for 10 h over NW6C5Z5 (Ni 10 wt.%, W: 6 wt.% with CeO_2ZrO_2 50 wt.%).

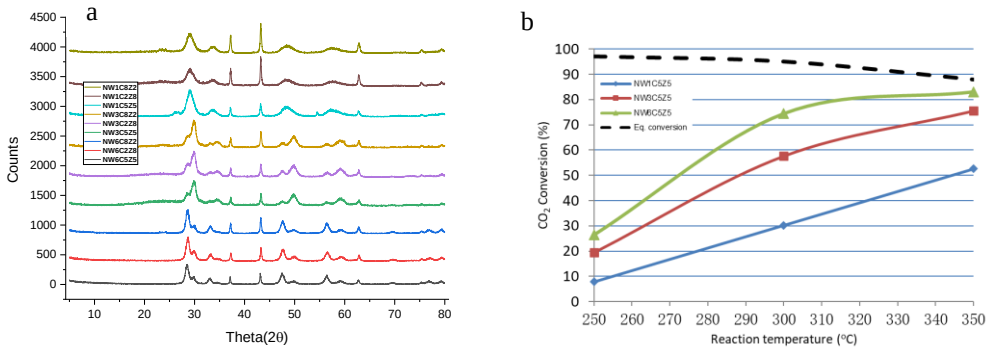

Fig 1. a. XRD patterns of prepared Ni-based catalysts and b. activity test results of the studied catalysts.

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CO_2 methanation over Ru and Ni based catalysts: towards a comprehensive kinetic model through a multi-technique study

Clara Larghi, Alessandro Porta, Roberto Matarrese, Carlo Giorgio Visconti* and Luca Lietti
Department of Energy, Politecnico di Milano, Milano 20156 (Italy)
**carlo.visconti@polimi.it*

Introduction. In the last years, the interest in CO_2 methanation has grown exponentially as it has proved to be a valid solution for both CO_2 reutilization and renewable energy storage. The most credited active metals for CO_2 methanation catalysis are Ru and Ni. The former is known to be the most active at low temperatures; however, because of its high cost, Ni is sometimes preferred despite its lower turnover-frequency (TOF) [1]. For these reasons, the metal loading in Ru-based catalysts is usually low (0.5-5 wt.%), while the amount of nickel required to achieve comparable performances is up to one order of magnitude higher. This work aims at developing a comprehensive kinetic model for CO_2 methanation on Ru and Ni catalysts through experimental data fitting and the exploitation of mechanistic information collected through *spatially-resolved operando* FT-IR spectroscopy and tests at short contact times.

Materials and Methods. Ru-based catalysts with loadings in the range 0.25-8 wt.% were prepared by dry impregnation of $Ru(NO)(NO_3)_3$ aqueous solutions on γ-Al_2O_3 (Sasol Puralox, d_p = 0.1 mm). Ni-based catalysts, with loading spanning from 5-88 wt.%, were prepared by dry-impregnation, deposition-precipitation or co-precipitation, starting from $Ni(NO_2)_3$ (hexahydrate) and γ-Al_2O_3 (Sasol Puralox, d_p = 0.1 mm) or $Al(NO_3)_3$ (nonahydrate). All the catalysts were characterized by H_2-TPR, N_2 adsorption isotherms, SEM-EDX, ICP-AES and H_2 pulse chemisorption, and tested at 0 barg, 150-390°C and space velocity in the range 10-130000 L(STP)/h/g_{cat}. The composition of the stream was quantified by an Agilent 990 micro-GC. *Spatially resolved operando* FT-IR measurements were taken at the inlet and outlet of a self-supporting catalyst wafer (GHSV = 125-850 L(STP)/h/g_{cat}) using a Bruker Vertex 70 FT-IR spectrometer, while analyzing the gas phase leaving the reactor by means of a MKS Multigas 2030 FT-IR spectrometer.

Results and Discussion. Through a first catalyst screening, the appropriate selection of precursors and preparation methods allowed us to exploit the structure sensitivity of the reaction, leading to materials with optimized average crystallite sizes: an impregnated 4% Ru/Al_2O_3 catalyst (TOF= 0.11 s^{-1} at 250°C, d_c = 5 nm) and a coprecipitated catalyst with an equimolar Ni/Al ratio (Ni 45 wt.%, TOF=0.03 s^{-1} at 250°C, d_c = 7 nm). In the two optimized samples, the difference in the intrinsic activity of the metals was effectively balanced by the overall metal loading, so that catalytic materials with similar active phase dispersion and activity a constant GHSV/g_{cat} were obtained (Figure 1a). Then, a set of dedicated tests was carried out at short contact times. Figure 1b shows the results obtained on the Ru-based catalyst: when reducing the contact time, the C-selectivity to CO pointed at 100% in the entire temperature range. The same trends were observed on the Ni-based catalyst, confirming that in both cases CO is a key intermediate. Coupling these results with the ones obtained by *spatially-resolved operando* FT-IR measurements, it was possible to formulate an appropriate kinetic scheme that can properly describe both the CO_2 consumption and CO formation (Figure 1c) on both Ru and Ni-based catalysts in a wide range of operating conditions.

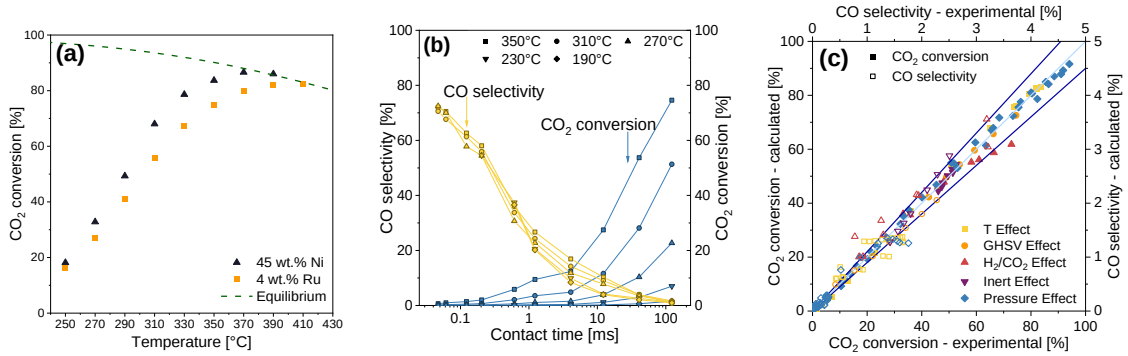

Figure 1. (a) CO_2 conversion of reference Ru and Ni catalysts; (b) CO_2 conversion and CO selectivity of reference Ru catalyst. P.C.: 0 barg, H_2/CO_2 = 4; (c) parity plot of CO_2 conversion and CO selectivity on Ru catalyst.

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BEA zeolite supported nickel catalysts for CO_2 methanation

W. Gac[1*], W. Zawadzki[1], G. Słowik[1], M. Kuśmierz[1], Y. Millot[2], L. Valentin[2], S. Dzwigaj[2**]

[1]*Faculty of Chemistry, Maria Curie-Sklodowska University, 3 M. Curie-Sklodowska Sq., 20-031 Lublin, Poland*
[2]*Laboratoire de Réactivité de Surface, Sorbonne Université-CNRS, UMR 7197, F-75005, Paris, France*
**wojciech.gac@umcs.lublin.pl, **stanislaw.dzwigaj@sorbonne-universite.fr*

Keywords: CO_2 methantion, BEA zeolite, nickel, deactivation

Introduction. Conversion of waste carbon dioxide with green hydrogen to the useful products, such as methane or methanol has been widely discussed as the method of greenhouse gas abatement together with renewable energy storage, as elements of the hydrogen economy. The methanation of CO_2 can be carried out at low temperatures by using relatively low-cost supported nickel catalysts [1,2]. However, nickel nanoparticles deposited on oxide supports may agglomerate during this exothermic reaction, leading to a decrease in catalyst activity. Moreover the traces of sulfur compounds in the feed stream can induce rapid and irreversible deactivation of the catalysts [3]. The aim of our studies was development of methanation catalysts with high activity, selectivity and improved resistance towards sintering and poisoning.

Experimental. The catalysts containing 10 wt.% Ni were preprated by the application of unmodiffied and dealuminated BEA zeolites as supports [4,5]. The properties of catalysts on the different operation stages were investigated by the application of versatile experimental methods, including X-ray diffraction, high-resolution transmission electron microscopy, FTIR, MAS NMR, NH_3 TPD [5]. The state of catalysts before and after reaction was investigated by quasi in-situ photoelectron spectroscopy (XPS) [5]. The course of reaction was determined by the application of in-situ diffuse infrared Fourier-transform spectroscopy (DRIFTS). The activity, selectivity and durability studies of catalysts in in the CO_2 methanation reaction were performed using fixed-bed continuous-flow quartz microreactor [5]. Similar studies were carried out for determination of H_2S poisoning resistance of catalysts.

Results and discussion. Reduction of catalysts prepared by the impregnation of unmodified BEA zeolite led to the formation of nickel nanoparticles of wide size distribution and versatile morphology, in part deposited on the external surface of zeolite grains. The increase in crystallite size and migration of nanoparticles to the outer part of grains with time-on-stream in the CO_2 methanation reaction performed at high temperature was observed. This resulted in the decrease in CO_2 conversion and selectivity towards methane. Such effects were attributed to relatively high hydrophilicity of the surface of unmodified BEA zeolite support. Stepwise poisoning of catalysts in the presence of the traces of H_2S in the feed stream led to the drop of CO_2 conversion and simultaneously to decrease in methane selectivity.

In turn, bounding of nickel precursor in the vacant sites formed upon zeolite dealumination resulted in the slower agglomeration of nickel nuclei and formation of very small metallic nanoparticles, nested only within zeolite grains. The obtained catalyst exhibited high activity, selectivity to methane and, at the same time, significantly improved sintering and H_2S poisoning resistance. TEM and XRD studies showed no decrease in crystallite size with time-on stream in CO_2 methanation reaction. The improved properties of catalysts were related to the higher dispersion of nickel, directly related to the increase in the number of active sites on metallic nickel crystallites, certain structural changes of the support, slowing down the agglomeration processes of the nickel crystallites, as well as changes in the surface properties of zeolite lattice, associated with a decrease in the acidity and hydrophilicity of surface.

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Ni supported on MnO catalysts for methane dry reforming

Huiyan Pan[1,2], Xiaowei Chen[1,*], Antonio Monzón[3], Juan José Delgado[1,*]

[1] *Departamento de Ciencia de los Materiales, Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cadiz, Campus Río San Pedro, Puerto Real (Cádiz), Spain*

[2] *Nanyang Institute of Technology, Nanyang, PR China*

[3] *Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza, Spain*

**Corresponding authors: xiaowei.chen@uca.es, juanjose.delgado@uca.es*

Introduction. Methane dry reforming with CO_2 (DRM) is considered as an alternative process to produce hydrogen. Plenty of efforts have been made using Ni-based catalysts on different supports, specially on alumina[1]. Until to now, only a few work reported Ni supported on manganese monoxide for this reaction[2]. A series of Ni-MnO catalysts with different Ni:Mn molar ratios have been synthesized. The objective is to understand the influence of Ni loadings on the catalytic activity for DRM.

Experimental. Ni-MnO catalysts have been synthesized using hydrothermal method. The synthesis was carried out on a custom-built six-port autoclave[3]. 50 mL of aqueous solution of 62.6 mM $KMnO_4$ and 3.13, 6.26, 15.65 or 25.04 mM $Ni(NO_3)_2$ was added to Teflon liner vessels. 5 mL of absolute ethanol was dropwise added to the above-mentioned solution. The autoclave was heated to 100 °C with a rotating speed of 50 rpm and kept at 100 °C for 12 h. The sample was dried overnight and calcined at 500 °C for 6 h. After reduction at 500 °C, the catalysts are named xNi-MnO (x=0.05, 0.1, 0.25 and 0.4). Catalytic test was performed using 50 mg of catalyst diluted by 100 mg of SiC. After pretreatment at 500 °C, the catalytic reaction was run at 750 °C for 24 h in a reaction mixture of 25 mL/min CH_4 and 25 mL/min CO_2.

Results and discussion. XRD results of these Ni-MnO catalysts indicate the formation of metallic Ni and MnO phases after reduction. ICP results show that the Ni loadings are very close to their theoretical values. Figure 1a shows CO_2 conversion of DRM over these reduced catalysts. The 0.25Ni-MnO catalyst exhibits the highest activity and the most stable CO_2 conversion among these Ni-MnO catalysts. Meanwhile, the highest H_2/CO ratio around 0.8 is observed over the same catalyst. The order of catalytic activity and H_2/CO ratio of these catalysts is as flowings: 0.25Ni-MnO > 0.1Ni-MnO > 0.05Ni-MnO > 0.4Ni-MnO.

The particle size of these catalysts is in a retively wide range up to 180 nm. Element maps of EDX results indicate that K partially covers Ni particles over 0.05Ni-MnO (Figure1b) and 0.1Ni-MnO catalysts, which is due to existence of potassium in cryptomelane phase before reduction. This might be the reason why these two catalysts present lower catalytic activitites than other catalysts. However, no K on Ni particles can be observed over 0.25Ni-MnO and 0.4Ni-MnO catalysts, which mainly consist of Mn_2O_3 and $NiMnO_3$ phases before reduction. Carbon nanofibers formed over Spent 0.25Ni-MnO catalyst after DRM reaction (Figures 1c and 1d) and it can be consumed during reaction.

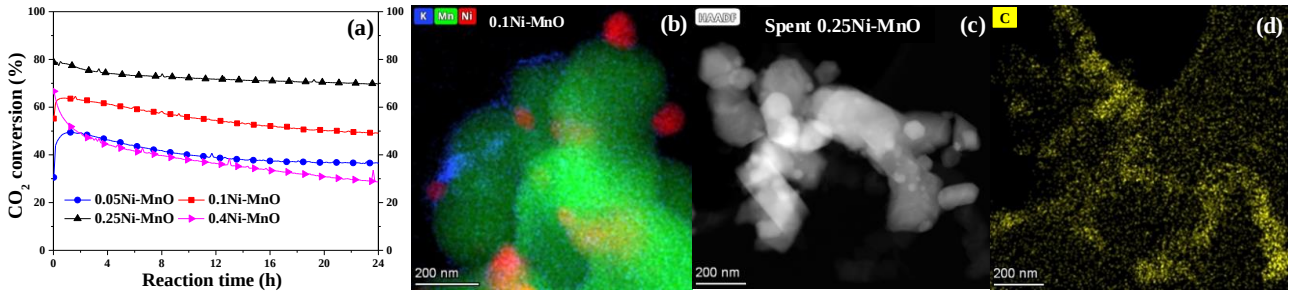

Figure 1. (a) CO_2 conversion of DRM over the Ni-MnO catalysts, (b) K, Mn and Ni maps of 0.1Ni-MnO catalyst, (c) STEM-HAADF image of Spent 0.25Ni-MnO catalyst and (d) C map of image (c).

Acknowledgments

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Integrated capture and methanation of CO_2 using mono- and bimetallic Ni and Ni-Ru catalysts along with a Na-Al_2O_3 sorbent

A. I. Tsiotsias[1], C. Giotas[1], A.I. Latsiou[1], N.D. Charisiou[1], M.A. Goula[1*]

[1]*Laboratory of Alternative Fuels and Environmental Catalysis (LAFEC), Department of Chemical Engineering, University of Western Macedonia, GR-50100, ZEP, Kozani, Greece*
[*]*mgoula@uowm.gr*

Keywords: CO_2 capture, CO_2 methanation, dual function materials, bimetallic catalysts.

Introduction. The conversion of emitted CO_2 into renewable methane aims to create a closed carbon cycle with net zero CO_2 emissions [1]. In recent years, the development of dual-function materials (DFMs) that can realize both functions of CO_2 capture and conversion to methane at the same temperature, in an integrated process, has gained increased traction [2]. Many of them utilize a physical mixture of sorbent and catalyst, as this approach enables the concurrent optimization of both active phases [2]. In this work, we employ mono- and bimetallic catalysts (Ni and Ni-Ru) supported on Pr-doped CeO_2, along with a Na_2O/Al_2O_3 sorbent, while varying the weight percentage of the catalyst in the DFM physical mixture.

Experimental/methodology. The 12% Na_2O/Al_2O_3 sorbent, 10% Ni/Pr-CeO_2 and 1% Ru, 10% Ni/Pr-CeO_2 catalysts were prepared via wet impregnation of the corresponding nitrate salts on a commercial Al_2O_3 support and a $Ce_{0.9}Pr_{0.1}O_{2-\delta}$ (Pr-CeO_2) support prepared via a modified Pechini method, respectively [1]. During the testing, 0.4 g of the dual-function material (sorbent-catalyst physical mixture in different weight ratios) was reduced under 10% H_2/Ar at 400 °C for 30 min, followed by temperature drop at 300 °C. 10% CO_2/Ar (50 ml/min) was then flown into the reactor for 15 min, followed by a 5 min Ar purge and finally, the flow was changed to 10% H_2/Ar (50 ml/min) for another 30 min (gas analysis via mass spectrometry).

Results and discussion. Figure 1 shows the evolution of the gas outlet CH_4 composition with time during the hydrogenation stage, following the CO_2 capture and Ar purge. It is essential to strike a delicate balance beween the supply of sorption and catalytically active sites, as both are needed during this integrated process. For example, 100 wt% of the Ni/Pr-CeO_2 catalyst alone yields only a meager amount of CH_4. CH_4 yield maxes out for 50 wt% Ni/Pr-CeO_2 catalyst at the DFM physical mixture at 0.41 mmol/g, while 0.33 mmol/g are produced for 25 wt% Ni/Pr-CeO_2 catalyst. It is also rational to think, that a lower catalyst amount results to obvious cost benefits. When the Ni-Ru bimetallic catalyst was tested, maximum CH_4 yield was observed for 25 wt% of NiRu/Pr-CeO_2 catalyst at 0.51 mmol/g, meaning that the more active bimetallic catalyst can boost CH_4 production while being in lower amounts at the DFM physical mixture.

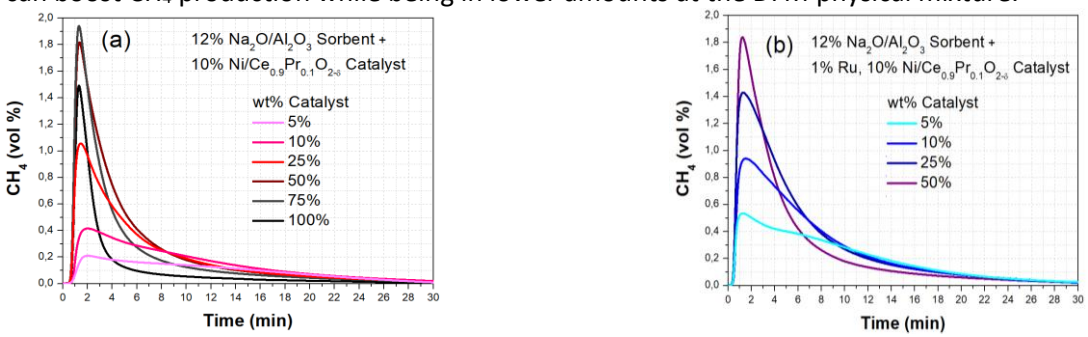

Figure 1: CH_4 yield during the hydrogenation stage for (a) Ni/Pr-CeO_2 and (b) NiRu/Pr-CeO_2 catalysts.

Acknowledgments

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Biogas upgrading through CO_2 methanation in a polytropic - distributed feed fixed bed reactor

P. Durán, P. Aragüés-Aldea, E. Francés, J.A. Peña, J. Herguido*

Catalysis, Molecular Separations and Reactor Engineering Group (CREG) - Aragon Institute of Engineering Research (I3A), Universidad Zaragoza, 50018 Zaragoza (Spain) * *jhergui@unizar.es*

Keywords: methanation, biogas, power to gas, distributed feeding, improved selectivity

Introduction. The conversion of CO_2 present in a raw biogas into more CH_4, using renewable-based hydrogen, could represent an interesting upgrading approach under the frame of *Power-to-Gas* (*PtG*) strategy. The involved *Sabatier* reaction is currently being studied woldwide, mainly using conventional catalytic fixed bed reactors. However, in a previous work [1] the alternative of a fixed bed polytropic-feed reactor (i.e., with several side gas inlets) was experimentally analyzed. It was found that a side distribution of CO_2 (so-called *'Poly-CO_2'* configuration) clearly led to improvements of performance in terms of both a conversion enhancement at all temperatures and a noteworthy lowering in selectivity to CO. The aim of this work is to extend the study to the methanation of a CH_4+CO_2 gas stream, simulating a biogas, and to compare it with the former results for a methane-free stream of CO_2.

Experimental/methodology. The experimental set-up was based on a 12 cm high fixed-bed reactor with different side feeding points and an upper main one. For a given WHSV (e.g., 108 $g_{CO2}.g_{cat}^{-1}.h^{-1}$) different feeding configuration were analyzed at different temperatures (400-250°C), always keeping the global ratios H_2:CO_2 = 4:1 and CH_4:CO_2 = 7:3. Apart from conversions and selectivities, the detailed temperature profile along the bed was also registered.

Results and discussion. The side distribution of biogas in the so-called *'Poly-Bio'* configuration (Fig. 1), always allowed a clear increase in activity, and also a flatter temperature profile, compared to the conventional co-feeding. In addition, for any achieved conversion the *'Poly-Bio'* arrangement always becomes less selective to CO than the conventional one, regardless of the working WHSV and chosen temperature (Fig. 2). Therefore, the previously observed advantages of distributed feeding [1] have also been achieved for biogas upgrading through CO_2 methanation.

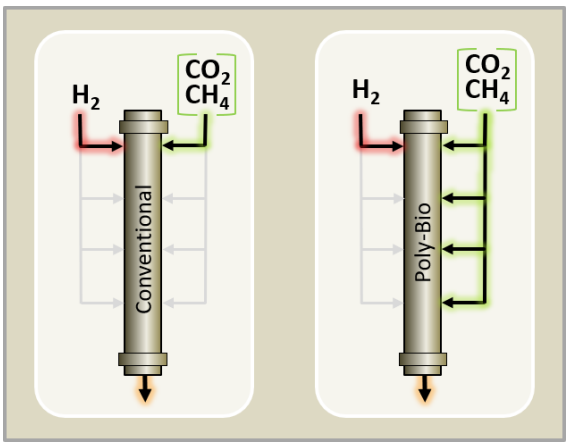

Fig. 1. Reactor sketch for *'Conventional'* and *'Poly-Bio'* feeding configurations.

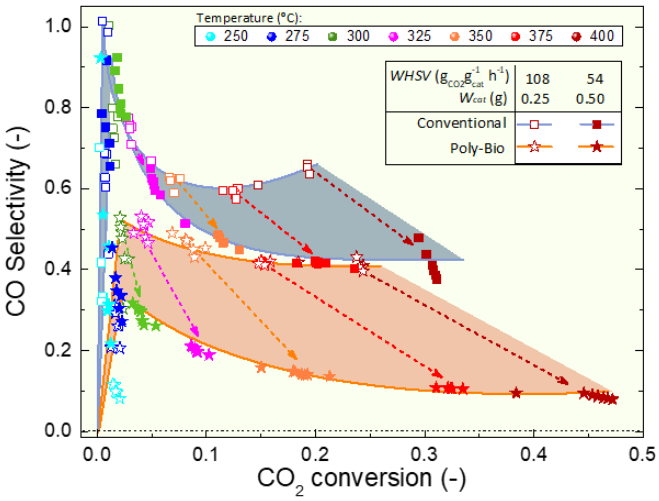

Fig. 2. Selectivity to CO *vs.* CO_2 conversion. Effect of *WHSV* as function of *T* (°C) and feeding mode.

Acknowledgments

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High C2-C4 selectivity in CO2 hydrogenation by particle size control of Co-Fe alloy nanoparticles wrapped on N-doped graphitic carbon

Lu Peng[1], Bogdan Jurca[2], Ana Primo[1], Alvaro Gordillo[3], Hermenegildo Garcıa[1], Vasile I. Parvulescu[2,*]

[1]Instituto Universitario de Tecnologıa Quimica, Universitat Politecnica de Valencia-Consejo Superior de Investigaciones Cientıficas, Av. De Los Naranjos s/n, 46022 Valencia, Spain
[2]Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Av., 030018 Bucharest, Romania
[*]vasile.parvulescu@chimie.unibuc.ro
[3]BASF SE, 67056 Ludwigshafen am Rhein, Germany

Keywords: Co-Fe alloy nanoparticles, N-doped graphitic carbon, selective CO2 hydrogenation to C2-C4

Introduction. Capture and utilization can be a viable strategy to decrease CO_2 atmospheric emissions, making it possible to reach the objectives for gradual decarbonization. Further, CO_2 hydrogenation can result in different compounds with different number of carbon atoms and functionalities. However, from the economic point of view, hydrocarbons with more than one carbon (C2+) are more attractive since they can be subsequently transformed into olefins or aromatics. Therefore, new catalysts for the CO_2 hydrogenation with an increased selectivity toward C2+ products are very important. With this aim, we report that Co-Fe alloy nanoparticles (NPs) of about 10 nm average size wrapped on N-doped graphitic carbon can exhibit selectivity toward C2, C3, and C4 over 50% under optimal conditions at CO_2 conversions over 30% [1].

Experimental/methodology. The N-doped graphitic carbon was obtained treating 400 mg chitosan in 250 mL acetic acid and 20 mL milli-Q water with an aqueous solution of sodium hydroxide (2 M, 500 mL). The resulted gel microspheres were then washed with distilled water to pH = 7. The resulting hydrogel microspheres were washed by a series of ethanol/water baths with an increasing concentration of ethanol and immersed in 40 mL $CoCl_2$-$FeCl_2$-ethanol solutions with different concentration, for 2 days. After that, the microspheres were reduced with 150 mL of $NaBH_4$-ethanol solutions and then exchanged by supercritical CO_2. The resulting aerogel microspheres were finally pyrolyzed under Ar flow at 900 C for 2 h.

Results and discussion. The resulted composites were fully characterized using textural, spectral, and diffractometric techniques (Figure 1, a). The reaction was structural sensitive with the highest selectivity to C2-C4 for catalysts with sizes in the range 10.5-14 nm (Figure 1, b). DFT calculations carried out at PBE-D3/def2-SVP level of theory taking 20 atoms with a composition Co14Fe6 prove the selectivity can be indeed controlled through the electron density by a strong interaction with the graphitic carbon support and fine-tuning of the particle size distribution (Figure 1, c).

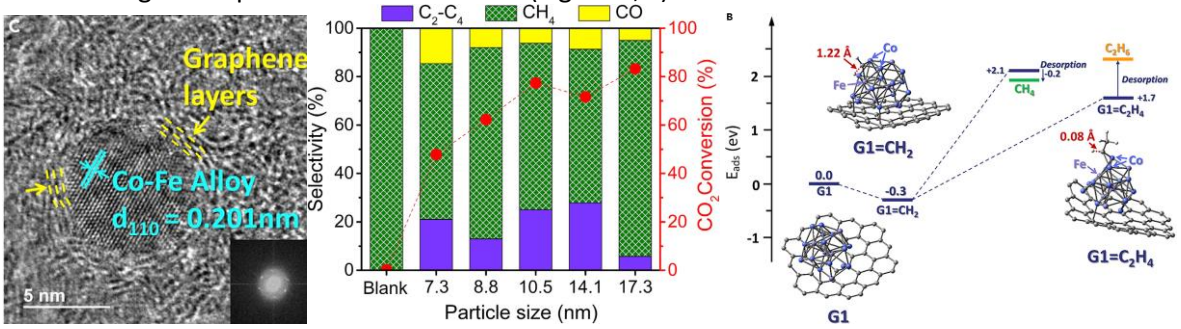

Figure 1. Structure of the graphitic catalysts (a), conversion of CO_2 and selectivity of the reaction (b) and DFT calculations (c)

In summary, this study has shown the importance of size control in Co-Fe NPs wrapped on N-doped graphitic carbon to favor the C-C bond formation during CO_2 hydrogenation.

Acknowledgments
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Article

High C2-C4 selectivity in CO2 hydrogenation by particle size control of Co-Fe alloy nanoparticles wrapped on N-doped graphitic carbon

vasile.parvulescu@chimie.unibuc.ro (V.I.P.)

hgarcia@upv.es (H.G.)

Highlights

Co-Fe nanoparticles wrapped on N-doped graphitic carbon catalyzes CO2 hydrogenation

Co-Fe@(N)Carbon affords 51% selectivity to C2-C4 hydrocarbons at 36% CO2 conversion

At H2/CO2 4, 300

C and 5

bar, a combined 30% of

CH2 = CH2 and MeCH =

CH2 is achieved

Particle size (10 nm) and

N-doping are crucial to

achieve high C2+

selectivity

Peng et al., iScience 25,

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Role of metal oxide and zeolite in the direct CO_2 hydrogenation to light olefins over bifunctional catalysts

S. Chernyak[1], M. Corda[1], M. Marinova[2], O. V. Safonova[3], V. Kondratenko[4], E. Kondratenko[4], V. V. Ordomsky[1] and A. Y. Khodakov[1]

[1]Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS, F-59000, Lille, France
[2]Univ. Lille, CNRS, INRAE, Centrale Lille, Univ. Artois, FR 2638 – IMEC, F-59000, Lille, France
[3]Paul Scherrer Institute, CH-5232 Villigen, Switzerland
[4]Leibniz-Institut für Katalyse e.V., Albert-Einstein-Str. 29a, 18059 Rostock, Germany

Introduction.

Carbon dioxide rational utilization is one of the most important goals for science and engineering, because of rapid climate changes and global warming caused by the increased anthropogenic emissions of this greenhouse gas. One of the possible solutions to control the atmospheric concentration of this gas is CO_2 hydrogenation to light olefins (LO) – platform molecules [1] for the synthesis of clean fuels, polymers and different organic molecules. The methanol-mediated approach implies CO_2 hydrogenation to LO over bifunctional catalysts containing a transition metal oxide for methanol synthesis and a zeolite for methanol to olefins (MTO) reaction [2]. This work is dedicated to the investigation of principal impact of each component in such catalysts on their final performance (activity, selectivity). For this purpose, a series of metal-oxide-zeolite hybrid catalysts were synthesised, characterized and tested in CO_2 hydrogenation and model reactions. Several general selectivity-conversion correlations have been uncovered for direct CO_2 hydrogenation to LO.

Experimental/methodology.

Zn-, In-, Mn-, Cr-, Ga- and Zr-based mixed oxides were synthesized by co-precipitation and impregnation and then calcined at 300-500°C. The obtained materials were physically mixed with several commercial SAPO-34 zeolites of different Si/Al ratio. The catalytic experiments were realized in both lab-scale three-microreactor setup and high throughput Avantium Flowrence unit at 375°C, 10-30 bar, 1-4 NL/h/g_{cat} and CO_2:H_2 ratio of 1:3. The catalysts were also tested in ethylene hydrogenation and methanol conversion at 375°C, 10 bar and different flow rates. The catalysts were characterized by XRD, XAFS, TPR and TEM-EDX. The mechanism and kinetics of CO_2 and H_2 activation were elucidated by temporal analysis of products (TAP).

Results and discussion.

The CO_2 hydrogenation over numerous synthesized catalysts showed a decrease in CO-free selectivity to LO fraction with increase in total yield of hydrocarbons (Figure 1). The conducted kinetic and characterisation experiments suggest that the metal-oxide part of bifunctional catalyst determines only the methanol/CO ratio but does not noticeably participate in the MTO process and secondary olefin hydrogenation reactions to paraffins. In opposite, acidity of zeolite part regulates the hydrocarbon selectivity and strong acid sites are responsible for hydrogen transfer reactions. These findings were further confirmed by TAP and model reactions. Ethylene hydrogenation tests were indicative of the crucial role of water and CO_2 in inhibition of olefin hydrogenation over metal oxides and hence of their very minor participation in the MTO reactions.

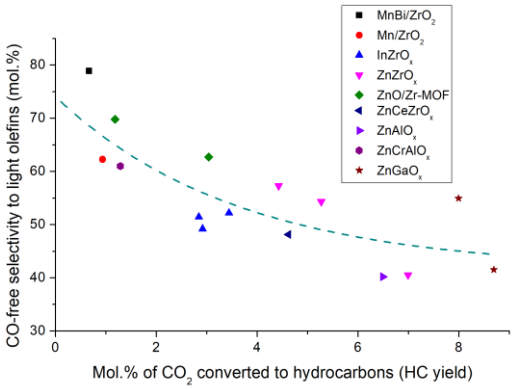

Figure 1. General dependence of CO-free LO selectivity on hydrocarbon yield for a variety of oxide-zeolite hybrid catalysts.

Acknowledgments

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Carbon Nitride-modified Support Materials for Cobalt-based Catalysts for the Hydrogenation of CO_2

A. Barthelmeß[1], M. Wolf[1*]

[1]*Karlsruhe Institute of Technology, Karlsruhe, Germany*
[*]*moritz.wolf@kit.edu*

Introduction. Carbon dioxide (CO_2) is a major contributor to climate change and its utilization as a feedstock is crucial in combating its effects.[1] Hydrogenation of CO_2 is a promising for the prodution of valuable hydrocarbons. Methanation of CO_2 has been demonstrated on a large scale while enabling utilization of existing natural gas distribution infrastructure.[2] Metal nanoparticles (MNPs) such as Ni, Fe, and Cu, supported on large surface area inorganic metal oxide supports, are commonly used as catalysts for this process. Previous research has shown the importance of well-designed interaction between the metal and support, which is crucial for catalyst activity, selectivity, and deactivation.[1]
Polymerized carbon nitride (C_3N_4) is gaining attention in catalysis research as a photocatalyst due to its unique properties, which make it also attractive as catalyst support material.[3, 4] The application of C_3N_4 as a support induces a change in the electron density at the catalytically active metal centers, which leads to increased chemical reactivity.[4] Furthermore, C_3N_4 has a high concentration of nitrogen and an abundance of incompletely condensed amino groups. The tertiary and aromatic amines may act as a Lewis base catalyst with numerous active sites. In the process of methanation, the Lewis acidic CO_2 carbon center can be targeted and the LUMO orbital can be filled through the transfer of electrons leading to a bent shape and loss of linearity, which ultimately leads to enhanced co-activation of CO_2.[3, 5]

Experimental/methodology. The conventional method for preparing C_3N_4 involves the polymerization of melamine, but typically results in low BET surface areas and non-porous systems.[4] In this study, we target the preparation of mesoporous C_3N_4 materials with different morphologies to investigate their applicability as support for the methanation of CO_2 when decorated with different metal nanoparticles. To improve the mechanical stability of the material, we coated commercial Al_2O_3 with C_3N_4. Additionally, the synthesis in molten salts resulted in mesoporous C_3N_4 samples.[6] The prepared C_3N_4(-modified) materials were then decorated with separately synthesized Co_3O_4 nanoparticles.[7]

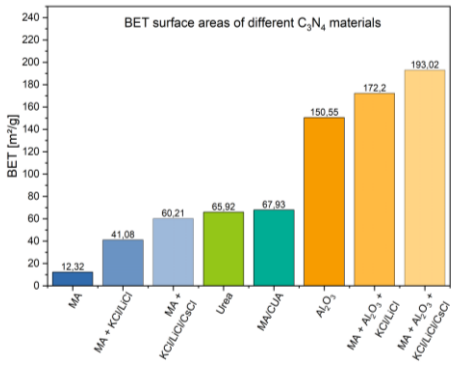

Fig. 1: BET surface areas of different C_3N_4 materials from various precursors (MA: melamine; CUA: cyanuric acid; urea) and preparation methods. After calcination at 550 °C, the coated Al_2O_3 samples contain 17 wt.% C_3N_4 derived from melamine.

Results and discussion. Analysis of the BET surface areas of the different materialsshowed a significant increase from bulk C_3N_4 to mesoporous C_3N_4 from the molten salt syntheses to Al_2O_3-coated structures (Fig. 1). Catalytic testing of a $Co/Al_2O_3@C_3N_4$ catalyst upon reduction in H_2 was conducted in a compact profile reactor[8] to study conversion of CO_2 to CH_4 and to identify potential synergetic effects of C_3N_4. The results indicate an accelerated conversion of CO_2 towards CO for C_3N_4-modified catalysts. Aside from the comparison of differently manufactured C_3N_4 supports to investigate the influence of surface properties and porosity, we have also produced C_3N_4 material in tubular form or as spheres.

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Switching the Selectivity of CO_2 Hydrogenation Over Supported Rh Catalysts by Phosphorous-loading

T. Shishido[1,2,3*], K. Fukuda[1], M. Li[1], H. Miura[1,2,3],

[1]*Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Hachioji, Tokyo, Japan*
[2]*Research Center for Hydrogen Energy-based Society, Tokyo Metropolitan University, Hachioji, Tokyo, Japan*
[3]*Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Kyoto, Japan*
[*]shishido-tetsuya@tmu.ac.jp

Keywords: CO_2 hydrogenation, Reverse water-gas shift reaction, Metal phosphode.

Introduction. Extensive efforts are needed to develop CO_2 utilization (Carbon recycling) technologies by using green hydrogen. Both the Sabatier reaction ($CO_2+4H_2 \rightarrow CH_4+ 2H_2O$) and the reverse water-gas shift (RWGS) reaction ($CO_2+H_2 \rightarrow CO+H_2O$) proceed competitively at ambient pressure [1]. To achieve the selective formation of CH_4 or CO by CO_2 hydrogenation, it is necessary to reveal the dominant factor for changing the selectivity in CO_2 hydrogenation. We found that the RWGS reaction proceeds selectively by phosphorus-loaded Rh catalyst while the Sabatier reaction proceeds mainly on Rh/TiO_2 (Fig. 1). In order to elucidate the role of phosphorus in CO_2 hydrogenation, phosphorus-loaded Rh catalysts were prepared and the relationship between structure and catalysis was investigated.

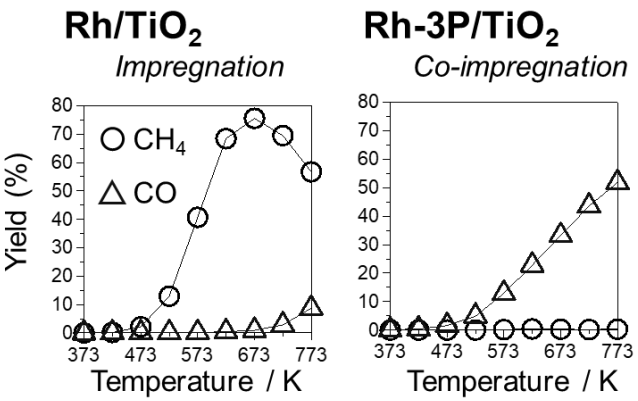

Fig. 1 CO_2 hydrogenation over Rh/TiO_2 and $Rh\text{-}3P/TiO_2$. $CO_2/H_2/N_2/He$ = 10/40/5/45 mL min^{-1}, GHSV = 60000 mL g_{cat}^{-1} h^{-1}

Results and discussion. The catalysts were reduced with H_2 at 673 K for 1 h prior to reaction and structural analysis. Rh K-edge XAFS analysis indicated that Rh phosphide (Rh_2P) was formed on $Rh\text{-}3P/TiO_2$. In addition, TEM and XRD results indicate that Rh_2P NPs were highly dispersed on $Rh\text{-}3P/TiO_2$. In Rh 3d XPS of catalysts reduced at 673 K, the binding energy for $Rh\text{-}3P/TiO_2$ is higher than that for Rh/TiO_2, indicating that the state of Rh in $Rh\text{-}3P/TiO_2$ and in Rh/TiO_2 are cationic and metallic, respectively. The band due to linearly adsorbed CO in the CO-DRIFT spectra was observed on Rh/TiO_2 (2082.3 and 2095.9 cm^{-1}) and (2085.5 and 2098.9 cm^{-1}), respectively. The peak position indicates that the C-O bond distance in adsorbed CO on $Rh\text{-}3P/TiO_2$ is shorter than that on Rh/TiO_2 by decreasing the π back-donation of the d-electron of Rh to the π^* orbital in the C-O bond. Therefore, the cleavage of C-O bond of CO molecule was strongly suppressed on $Rh\text{-}3P/TiO_2$. In fact, no CO hydrogenation took place on $Rh\text{-}3P/TiO_2$. The H_2/D_2 exchange reaction was performed at 298 K to evaluate the H_2 activation ability. $Rh\text{-}3P/TiO_2$ exhibited a higher exchange rate than Rh/TiO_2. Based on the kinetic analysis, the reaction orders of H_2 and CO_2 were estimated to be 0.7 and 0.0 for $Rh\text{-}3P/TiO_2$, and 0.0 and 1.3 for Rh/TiO_2, respectively. These results indicate that the rate-determining step (RDS) of CO_2 hydrogenation to CO over $Rh\text{-}3P/TiO_2$ would be the reaction process involving CO_2 (adsorption or activation). In the case of Rh/TiO_2, the activation of H_2 or the bond formation (C-H or O-H) processes is the RDS to form CH_4.

We have successfully controlled the selectivity of CO_2 hydrogenation by adding phosphorus to the supported Rh catalyst. CO was produced with 100% selectivity on the P-loaded catalyst. Structural analysis revealed that rhodium phosphide NPs (Rh_2P NPs) were formed on the P-loaded catalyst. The cationic Rh species in Rh_2P were found to selectively produce CO by preventing the cleavage of the C-O bond of the CO molecule.

Acknowledgments *A part of this work was the Tokyo Metropolitan Government Advanced Research Grant Number (R3-1).*

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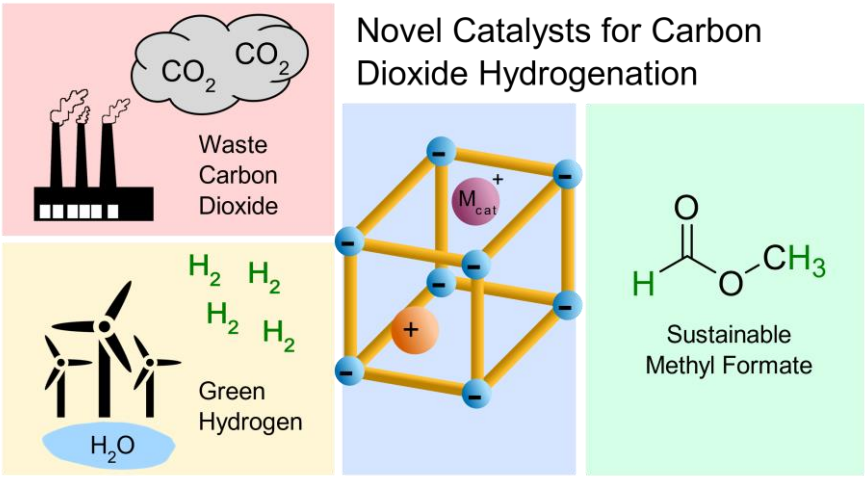
Selective CO_2 Hydrogenation to Methyl Formate using CO_2 as the Sole Carbon Source

Roland C. Turnell-Ritson[1,*], Paul J. Dyson[1]

[1]*École polytechnique fédérale de Lausanne, Lausanne, Switzerland*
[*]*roland.turnell-ritson@epfl.ch*

Keywords: CO_2 hydrogenation, methyl formate, zeolites, sustainability

Introduction. Atmospheric concentration of CO_2 is still increasing, despite international efforts to curb emissions. The removal of CO_2 from the atmosphere is a high cost endeavour, necessitating economic incentives for carbon capture. More importantly, the use of the near-unlimited C_1 resource of atmospheric CO_2 as a building block for process chemicals is essential to a sustainable future.[1] We have developed efficient catalysts for the hydrogenation of CO_2 to formic acid (FA), methanol and CO. Additionally, we have combined these C_1 building blocks into methyl formate (MF) in one pot. Our catalysts are based on the encapsulation of noble metal complexes and sub-nanoparticles in the pores of zeolites, leveraging the acidity of the support and the principle of nanoconfinement to accelerate these multi-step reactions.



Experimental/methodology. Noble metal precursors were encapsulated within the pores of zeolites, and subsequently manipulated *via* reduction, oxidation, or "ship-in-a-bottle"-type synthesis to generate the active catalyst. Catalytic hydrogenation of CO_2 was performed in a batch reactor below 250°C with pressures in the range 20-100 bar. The product selectivity can further be tuned using various solvents.

Results and discussion. A Ru-based catalyst was developed for the hydrogenation of CO_2 to FA, and simultaneously facilitates fast esterification to MF (TOF > 60 h^{-1}), comparable to similar catalysts which operate at higher temperatures and pressures.[2,3] A second series of catalysts, both from the literature and developed in our lab, are capable of CO_2 and FA hydrogenation to MeOH under the applied conditions. Combining two appropriate catalysts, MF in which both C atoms derive from CO_2 is formed. In the presence of a methoxide additive, the MF can be decarbonylated to give high CO concentrations (>20%) at a much lower temperature than traditional reverse water gas shift reactions.[4] The structures of these catalysts will be discussed, and the reaction mechanisms will be explored to understand the key catalyst features which enable their reactivity. The present work allows the formation of three major C_1 synthons widely used in industry using CO_2 under relatively mild conditions at accelerated rates. Further, attempts to couple CO_2 hydrogenation with C-C bond-forming reactions will be described, as we progress towards the sustainable and selective synthesis of C_{2+} products from atmospheric carbon.

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Selectivity control between Reverse Water-Gas Shift and Fischer-Tropsch Synthesis in Iron-based Catalysts for CO_2 Hydrogenation

Weixin Meng[1,2], B. C. A. de Jong[1,2], G. L. Bezemer[3], H. J. Heeres[1], Jingxiu Xie[1*]

[1] *Green Chemical Reaction Engineering, Engineering and Technology Institute Groningen, University of Groningen, Groningen, the Netherlands*

[2] *Equal contribution*

[3] *Energy Transition Campus Amsterdam, Shell Global Solutions International B.V., Grasweg 31, 1031 HW Amsterdam, the Netherlands*

[*] *Corresponding Author's E-mail address: jingxiu.xie@rug.nl*

Keywords: CO_2 conversion, Fischer-Tropsch Synthesis, Reverse Water-Gas-Shift, C_{5+} hydrocarbons

Introduction. Converting CO_2 and renewable H_2 into valuable chemicals and fuels would simultaneously decrease CO_2 emissions and displace fossil resources. CO_2 hydrogenation to hydrocarbons (CO_2-FTS) requires the reduction of CO_2 to CO via the reverse water gas shift (RWGS) reaction followed by the conversion of CO to hydrocarbons via the Fischer-Tropsch Synthesis (FTS) reaction[1]. The iron-based catalyst is a promising starting point as a bifunctional catalyst for CO_2-FT, due to its ability to catalyze both reactions[2]. The delicate balance between the RWGS and FTS reactivities is a challenge to maximize long chain hydrocarbon (C_{5+}) selectivity. Both RWGS and FTS are structure sensitive and this study aims to investigate the influences of iron nanoparticle size and dispersion on the interplay between RWGS and FTS.

Experimental/methodology. The carbon-supported iron-based catalysts with 5 %, 10 %, and 20 % iron weight loading (with potassium promoter) were prepared by incipient wetness impregnation. N_2 physisorption, XRD, H_2-TPR, ICP-OES, and TEM were used to identify the chemical and physical properties of the catalysts. Prior to the reaction in a fixed-bed reactor, the catalysts were reduced with diluted H_2 flow at 400 °C for 2 h, followed by H_2/CO carburization at 280 °C for 20 h. After reduction and carburization, the catalysts were evaluated at 300 °C, 11 bar, H_2/CO_2 = 3, 1500 - 18000 h^{-1}. The products were analyzed by online with a GC equipped with TCD and FID.

Results and discussion. From TEM, the average particle sizes of the carburized catalysts with different iron loading were 8 - 11 nm. The figure provides an overview of the catalytic performance at 300 °C, 11 bar, H_2/CO_2 = 3, 1500 - 18000 h^{-1}. At 16 % CO_2 conversion, CO selectivity was >92 % for all catalysts, suggesting that RWGS was the primary and dominating reaction. At 35 % CO_2 conversion, CO selectivity decreased to <30 %, confirming that FTS was the secondary reaction and CO_2-FT proceeds via CO. At both conversion levels, the catalyst with a higher iron loading and larger average Fe particle size produced more hydrocarbons. A possible explanation is the presence of more terrace sites which enhance the CO adsorption and stabilize CH* species, thereby promoting C-C coupling[3]. This contribution will discuss separately the effect of particle size and dispersion, so as to unravel the origin of structure-sensitivity in the CO_2-FTS process.

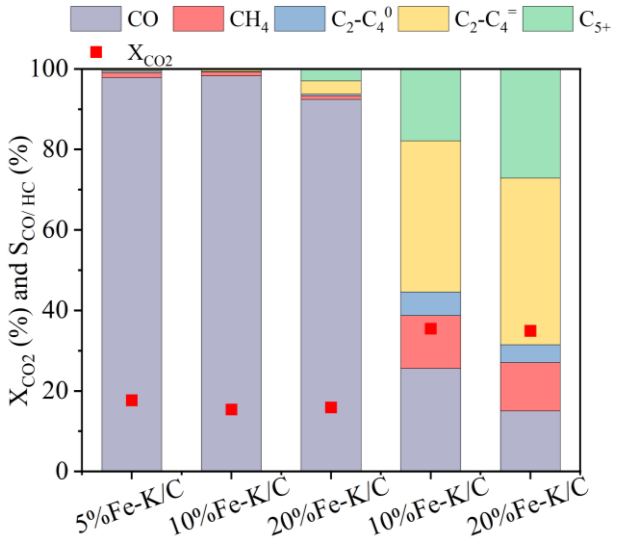

Figure. CO_2 hydrogenation performance over different catalysts at CO_2 conversion = 16% and 35%.

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Hydroformylation with CO_2 through combined homogeneous and zeolite catalysis

H. Van Dessel[1], S. Van Minnebruggen[1], C. Marquez[1], D. De Vos[1*]

[1]*Centre for Membrane Separations, Adsorption, Catalysis and Spectroscopy for Sustainable Solutions (cMACS), KU Leuven, 3001 Leuven, Belgium*

[*]*dirk.devos@kuleuven.be*

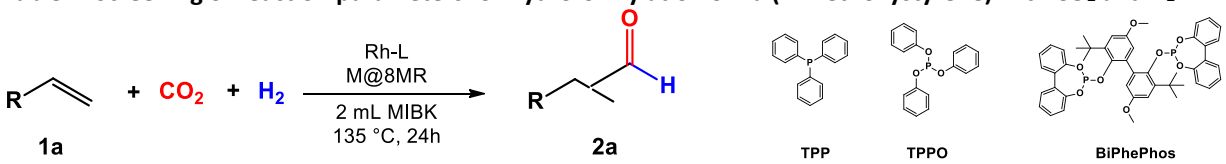
Keywords: Reverse water-gas shift, Small-pore zeolite, Hydroformylation

Introduction. The hydroformylation of olefins to aldehydes is one of the largest homogeneously catalyzed processes used in industry, with an annual production exceeding 10 Mton.[1] Given its large scale, using CO_2/H_2 as a syngas surrogate for this reaction would avoid the use of toxic CO and valorize CO_2 into valuable chemicals using green H_2. Combining the CO_2 reduction towards CO (reverse water-gas shift reaction) with a CO-consuming reaction (e.g. hydroformylation) in a one-pot system creates several incompatibilities regarding their respective reaction conditions, like the hydrogenation of the alkene and the instability of the homogeneous catalyst at the unusually low $CO:H_2$ ratios. In this work, these limitations were overcome by using two catalysts using a one-pot system: a metal-loaded small-pore zeolite for the RWGS, and a homogeneous Rh(I)-phosphine catalyst to perform hydroformylation.

Experimental/methodology. Zeolite catalysts were synthesized according to literature.[2,3] Reactions were performed in stainless steel autoclaves (10 mL). The gas phase was monitored using gas phase FTIR. The reaction mixture was analyzed with GC-FID, using *n*-decane as internal standard for quantification.

Results and discussion. Different metal loaded small-pore zeolite catalysts were screened for RWGS under conditions closely related to hydroformylation. The encapsulation of noble metals in the small-pore zeolites was then assessed in comparative hydrogenation experiments. The best performing zeolite was finally used in one-pot hydroformylation experiments with only CO_2 and H_2. Initial screening of reaction conditions of combined reactions is shown in Table 1. Matching of the reaction rates for RWGS and hydroformylation is key to achieve high TON as a low RWGS-rate results in Rh-catalyzed substrate hydrogenation. The zeolite catalyst is essential (entry 1), as no CO or hydroformylation products were observed in its absence. The triphenylphosphine (TPP, entry 2) ligand outperformed its phosphite alternative (TPPO, entry 3) and the bulky chelating BiPhePhos ligand (entry 4). Summarizing, suitable metal@8MR catalysts allow sufficient RWGSR in conditions compatible with those needed by the carbonylation catalyst. Thus, the 2-catalyst system successfully enables hydroformylation with CO_2 as the carbon building block.

Table 1. Screening of reaction parameters for hydroformylation of 1a (4-Methoxystyrene) with CO_2 and H_2.



Entry	L (L/Rh)	pCO_2	pH_2	TON_{Rh}
1[a]	TPP (100/1)	15	5	0
2	TPP (100/1)	15	5	188
3	TPPO (10/1)	15	5	15
4	Biphephos (5/1)	15	5	0

Reaction conditions: 4-Methoxystyrene **1a** (0.4 mmol), $Rh(acac)(CO)_2$ (0.4 µmol), ligand (0.002 – 0.04 mmol), 250 mg M@8MR, 2mL MIBK, 24 h and 135 °C. [a] No zeolite was added.

Acknowledgments

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The reactivity of oxygen vacancies of CeO_2-based mixed oxides toward CO_2 deoxygenation to CO

Nan-Chien Chiang, Ruo-Yun Lin, Chin-Ting Huang, Tzu-Hsun Tsai, Tz-Jie Ju,. Shawn D. Lin[1*]

[1] *Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan*

[*] *sdlin@mail.ntust.edu.tw*

Keywords: CO_2 utilization, mixed oxide, oxygen vacancy

Introduction. CO_2 capture and utilization is a must for easying the global warming caused by the uses of fossil fuels. The direct deoxygenation of CO_2 to CO is one possible route and the similar deoxygenation route may also convert H_2O to H_2. Previous works demonstrate this thermal deoxygenation route over oxygen vacancies of CeO_2 at temperatures above 700 °C. [1-3] The vacancy formation temperature and the deoxygenation reaction temperature will govern the energy demand for such CO_2 utilization approach. A deoxygenation temperature at mid-temperature range is desirable which can lead to integration with oxygen-conducting inorganic membrane to facilitate sustainable CO_2 utilization process. CeO_2-based mixed oxides are known to have dopant-dependent properties of oxygen vacancies which can possibly govern the reactivity for CO_2 deoxygenation. In this study, various CeO_2-based mixed oxides are prepared by coprepreciptaion and their reactivity toward CO_2 deoxygenation is evaluated.

Experimental/methodology. The mixed oxides were all prepared from nitrate precursors using a coprecipitation method at a constant pH of 12 maintained by NaOH addition, named as M-CeO_2. The filtered solid was dried and then calcined to 700 °C. The prepared samples were analyzed by sequential TPR (under 10% H_2/N_2) and TPRx-CO_2 (under 5 % CO_2/Ar), both from 50 °C to 700 °C at a ramp rate of 5 °C/min, using a housemade microreactor system equipped with TCD and MS detection of effluent stream.

Results and discussion. The mixed oxides examined include Zr-, Gd-, Sm-, Fe-, Co-, Cu-, and In-CeO_2. The commonly used oxygen ion conductors, Sm- and Gd-CeO_2, did not show significant CO_2 deoxygenation activity in sequential TPR and TPRx-CO_2 tests, neither did Zr-, Cu-, or Co-CeO_2. Fe- and In-CeO_2 showed reactivity for mid-temperature CO_2 deoxygenation under the test conditions, with a calculated CO yield above 90 % (based on consumed CO_2). XRD analyses indicate that Fe_2O_3 and In_2O_3 phase were present in the prepared mixed oxides, reduced Fe^0 and In^0 phases could be identified after TPR, and the oxide phases were found again after TPRx-CO_2. Furthermore, the reactivity of both Fe- and In-CeO_2 incresed with increasing Fe and In percentage in mixed oxides. This indicates that Fe- and In-related crystallites played an imporatant role in CO_2 deoxygenation. Comparatively, neither the physical mixture of CeO_2 and Fe_2O_3 nor the Fe_2O_3 supported on SBA15 offered the same reactivity. This suggests the presence of Ce-Fe (Ce-In) interaction. The isothermal CO_2 deoxygenation over $Ce_7Fe_3O_y$ at 600 °C was also examined, wherein the reactivity was enhanced by 50 % when $Ce_7Fe_3O_y$ powders were put over a 1.6-mm-thick stand-alone GDC (Ga-doped CeO_2) membrane within an in-house-made membrane reactor. This indicates the feasibility of integrating CO_2 deoxygenation mixed oxide with oxygen conducting membrane at mid-temperature range, as a viable CO_2-to-CO utilization process.

Acknowledgments

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Dual Function Material Design for Circular Methanol Economy

A. Ipek Paksoy[1], Ali Goksu[1], Tomas Ramirez Reina[1,2], Melis S. Duyar[1*]

[1]*School of Chemistry and Chemical Engineering, University of Surrey, Guildford, GU2 7XH United Kingdom*
[2]*Inorganic Chemistry Department & Material Science Institute, University of Seville-CSIC, Sevilla, España*
[*]*m.duyar@surrey.ac.uk*

Keywords: dual function material, integrated carbon dioxide capture and utilization, circular economy

Introduction. The alarming increase in CO_2 emissions, mainly due to fossil fuel consumption, creates an urgent requirement for CO_2 reduction. Thus, the novel concept of integrated carbon capture and utilization (ICCU) has gained interest considering environmental and industrial aspects. [1] Dual Function Materials (DFM), containing sorbent species that selectively adsorb CO_2 and a catalyst that utilizes it, can be successfully implemented in this concept near a renewable H_2 generation facility to reduce both the economic and energy requirements. [2] Therefore, sustainable CO_2 valorization can be achieved with the production of chemical fuels and value-added chemicals. [1] Herein, methanol stands out as an appealing end-product considering its high energy density to be used as transport fuel. Methanol can also be used as a building block for other chemicals required in industry. [3]
In this context, this work aims to design appropriate DFMs to produce methanol from captured CO_2.
Experimental/methodology. DFMs are prepared using Ca, K, and Na as CO_2 adsorbing species, and Ni and Ga for catalytic CO_2 hydrogenation to methanol. Preparation of the samples involves supported adsorbent preparation followed by the impregnation of catalytic materials. The required amounts of the SiO_2 support and $NaNO_3$, KNO_3, or $Ca(NO_3)_2{\cdot}4H_2O$ are mixed with deionized water at room temperature with a magnetic stirrer. The excess water is removed in a rotary evaporator under reduced pressure. The samples are dried overnight at 120 °C and calcined at 400 °C for 4 hours. The required amounts of $Ni(NO_3)_2{\cdot}6H_2O$ and $Ga(NO_3)_3{\cdot}xH_2O$ are mixed with the supported adsorbent and deionized water. Excess water is removed in a rotary evaporator under reduced pressure and samples are dried overnight at 120 °C.
The DFMs are reduced at 700 °C under pure H_2 flow prior to the catalytic tests. Carbon dioxide capture and utilization tests are performed on a tubular fixed-bed quartz reactor at atmospheric pressure varying temperature and flow rates of CO_2 and H_2. The preliminary results are analyzed via a mass spectrometer.
Results and discussion. NiGa-Ca/SiO_2 sample starts producing methanol under H_2 flow even in TPR during temperature programmed surface reaction tests. Although the observed amount is low in concentration, the result is important as it can be seen as an indication of DFM adsorbing CO_2 from the ambient atmosphere and converting this to methanol in H_2 flow at 300 °C (Figure 1).

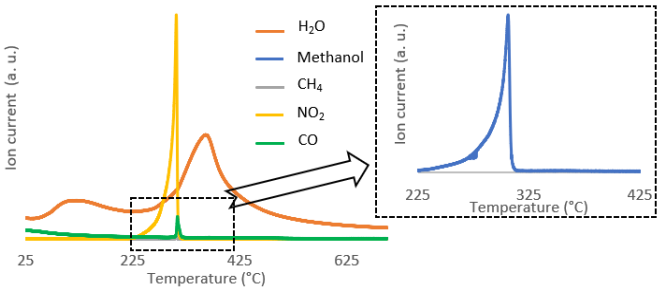

Figure 1. Ion current vs temperature data during TPR for NiGa-Ca/SiO_2.

Thus, the preliminary results revealed that methanol can be produced on the NiGa phase of the DFM from captured CO_2. More catalytic and characterization tests are required to determine the activity and selectivity of DFMs for carbon dioxide hydrogenation to methanol.

Acknowledgments
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Dyes as efficient metal-free catalysts for the synthesis of cyclic carbonates through the reaction of CO_2 cycloaddition to epoxides

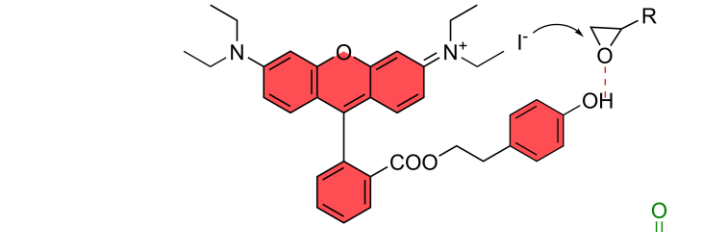
J. Chen[1*], P. P. Pescarmona[2]

[1, 2] *Chemical Engineering Group, Engineering and Technology institute Groningen (ENTEG), University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

[*] *Jing.Chen@rug.nl*

The utilisation of CO_2 for the synthesis of value-added chemicals has gained increasing interest for the past decade.[1] One promising method is atom-economically transferring CO_2 and epoxides into cyclic carbonates relevant to a wide range of applications as green solvents, lithium-battery electrolytes, intermediates for organic synthesis, and monomers for preparation polymers.[2] The novel organocatalysts are synthesised by modification of the conventional halide salts or ionic liquids with hydrogen bond donor (HBD) groups, which can activate the epoxides by forming hydrogen bonds with the oxygen atom of epoxide, facilitating the ring-opening step of the nucleophiles.[3]

In this project, we selected three large-scale available dyes, rhodamine B (RhB), rhodamine 6G (Rh6G) and methylene blue (MB), which contain a big xanthene core and a chloride anion as a nucleophile. These three dyes were first ion-exchanged with KX (X= Br, I) to obtain a set of nine organocatalysts (dye-X, X = Cl, Br, I). Their catalytic activity was tested in converting CO_2 and styrene oxide into styrene carbonate at 80 °C, 10 bar CO_2 for 24 hrs. The structure of the cation, the nature of the anion and the effect of adding H_2O as an external HBD compound on the catalytic activity of dyes were comprehensively investigated. Their catalytic activity largely depends on the counterpart anions, decreasing from I^- > Br^- > Cl^-. Additionally, a vast improvement in catalytic activity was achieved by adding 50 mg H_2O as an external HBD compound (96 % styrene carbonate yield with RhB-I and Rh6G-I). However, these dyes are inefficient under lower reaction temperatures (45 °C). Therefore, the new organocatalyst of RhB-Ethyl-PhOH-I (Figure 1) was synthesised and obtained 41 % styrene carbonate yield under mild reaction conditions (45°C, 10 bar CO_2, 18 h). Moreover, the organocatalyst of RhB-Ethyl-PhOH-I among the selected epoxide substrates achieved satisfactory corresponding cyclic carbonate yields (Figure 1). Nanofiltration simulated the catalyst recovery, demonstrating a high efficiency of catalyst separation. The organocatalysts of RhB-Ethyl-PhOH-I possess the advantages of efficient catalytic activity, straightforward synthesis method, and ease of separation from the product, which are all assets for the potential for large-scale applications.



R	Yield / %
Methyl	84
Chloroethyl	53
Allyl methyl ether	75
Benzene	49
Hexyl	46

Figure 1. The catalytic activity of RhB-Ethyl-PhOH-I

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Insight the Ti nanotubes array nanostructure and its role on the electro reduction of CO_2-derived oxalic acid (OX)

Francesco Pio Abramo[1], Federica De Luca[1], Angelica Chiodoni[2], Gabriele Centi[1], Gianfranco Giorgianni[1], Siglinda Perathoner[1], Salvatore Abate[1]

[1]*Department of ChiBioFarAm (Industrial Chemistry), University of Messina, ERIC aisbl and INSTM/CASPE, V.le F. Stagno d'Alcontres 31, Messina 98166, Italy*
[2]*Center for Sustainable Future Technologies @ POLITO, Istituto Italiano Di Tecnologia, via Livorno 60, Turin, 10144, Italy*

Keywords: Oxalic acid; TiO_2 nanotubes; Breakdown; oxygen bubble evolution; Glyoxylic acid; Glycolic acid; Electrocatalysis.

Introduction.

The production of CO_2-derived chemical feedstocks, coupled with the use of renewable energy, is the challenge of the current century to mitigate the climate change. In this scenario, the electrocatalytic hydrogenation of) in glycolic acid (GC) and/or Glyoxylic acid (GO,) is one of the most important pathways for the conversion in C2+ valuable chemicals. TiO_2 nanotubes (NTs) are very promising electrocatalysts due to their low toxicity and robustness. However, their low productivity makes this route far from commercialization, and their optimization is highly desired [1]. In this work, the experimental conditions were changed to reach the breakdown potential and to study the effect of the TiO2 NTs nanostructure on the catalytic activity and selectivity. Moreover, a thermal and electrochemical pre-treatment were used to obtain a more uniform TiO2 NTs structure and limit the over-etching of NTs during anodization.

Experimental/methodology.

Several electrodes were prepared by anodic oxidation of titanium foils varying the applied potential (50 V, 60 V) and the anodizing time (15 min, 60 min). NTs were grown by (i) on as received washed Ti foils, (ii)on thermally (annealing at 450°C for 30 minutes), or (iii) on electrochemically (anodization at 20V for 2 hours in H_2SO_4) pre-treated Ti foils.

Results and discussion.

The nanostructure was investigated by SEM and discussed in relation to the anodization curves. Longer and rougher NT array are clearly visible for the sample anodized at 60 V compared to the samples obtained at lower potential, suggesting that breakdown conditions are achieved (the anodization current increase) [2]. The NTs array of the electrochemical pre-treated sample is the longest among all investigated samples, and their walls are visibly rougher, probably due to the oxygen bubbles release during the growth process [3]. Roughness and length of NTs walls influence the activity of the catalysts. Indeed, a linear correlation among the NTs length, the selectivity to GC and OX conversion is observed, indicating the NTs length as a critical factor in the electrochemical process. On the other hand, the roughness of the NTs walls could be useful to increase the Faradaic efficiency to GC (FE_{GC}) while more smooth nanotubes favour the GO formation. In addition to the effect of the rougher nanostructure on performance, the role of defective oxygen vacancies, due to Ti^{3+} auto doping, measured by X-ray photoelectron spectroscopy (XPS) and confirmed by cyclic voltammetry (CV), was demonstrated by the linear correlation with OX conversion and NT length.

By varying the electrodes nanostructure, it is therefore possible to tune the glycolic acid to glyoxylic acid relative ratio. The best FE_{GC} (86%) and OX conversion (48%) were obtained at -1,1V for electrochemically pre-treated sample.

Acknowledgments

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Production of eChemicals and eFuels using eREACT™

S. De Sarkar[1*], P. M. Mortensen[1], K. A. Petersen[1]
[1]*Topsoe, Haldor Topsøes Allé 1, Kgs. Lyngby, 2800, Denmark*
[*]*suds@topsoe.com*

Keywords: eREACT™, RWGS, eFuels, CO_2 utilization

Introduction. Topsoe's eREACT™ technology is an excellent example of a step change towards a more sustainable future. It enables direct electrification of the chemical industry by replacing fossil-based energy sources with renewable energy [1]. Many potential applications of eREACT™ have been identified, making it a 'platform' technology. Among these, the eREACT™ for reverse water gas shift (RWGS) can be used to valorize CO_2 and biogas, enabling electrofuels (eFuels) production.

Experimental/methodology. The proof-of-concept for eREACT™ was established using a bench-scale reactor for steam methane reforming (SMR) and reverse water gas shift (RWGS) applications. The bench-scale eREACT™ reactor has been successfully scaled up to a pilot plant. A number of demonstration runs of eREACT™ with various feed compositions and operating conditions have been carried out in the pilot plant confirming the scale up of the technology.

Results and discussion. Tests in the bench-scale eREACT™ reactor for SMR confirmed the desired operation with very low methane slip at the reactor outlet at temperatures of 900°C-950°C. For eFuels applications, RWGS experiments were conducted successfully at 1000°C and above, producing syngas with the target H_2/CO ratio suitable for downstream synthesis processes [2].

The pilot operation of eREACT™ with various feed compositions, including biogas (60 mol% CH_4; 40% mol% CO_2), has been conducted successfully by long-term operation [3]. The expected catalytic performance has been confirmed through various tests, including operation cycles resembling transient conditions during industrial operations.

Process development activities around sustainable aviation fuels (SAF) production, using eREACT™ for RWGS via Fischer-Tropsch (FT) route, has revealed several advantages, including very high carbon efficiency and close to the theoretical minimum hydrogen feed consumption. This means that the electrolysis unit, producing the renewable hydrogen upstream of the eREACT™, can be made as small as possible, thus minimizing capital investment. Furthermore, it results in significantly less overall power consumption in eREACT™ scheme than that in other processes, including the non-electrical RWGS process utilizing either selective or non-selective RWGS catalysts. Additionally, the eREACT™ technology provides synergy in the FT-based eFuels process by allowing conversion of the recycled off-streams from downstream units maximizing the carbon dioxide feed utilization (>95%) in eREACT™ based eFuels process while minimizing the overall power consumption per unit of product.

Acknowledgments
This research is partially financed by the Energy Technology Development and Demonstration Program (EUDP) in Denmark under the project 64019-0014 entitled "eSMR-MeOH: Biogas to MeOH by electric reforming" as well as Innovation Fund Denmark (IFD) under file no. 1044-00133B.

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Electrocatalytic behaviour of CuS_x-Bi nanocrystals in CO_2 reduction using new engineered artificial leaf-type devices

D. Giusi[1], A.M. Ronsisvalle[1], C. Genovese[1], M. Miceli[1], G. Centi[1], S. Perathoner[1], C. Ampelli[1*]

[1]*Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm), University of Messina, ERIC aisbl and CASPE/INSTM, Messina, Italy*
[*]*ampellic@unime.it*

Keywords: CO_2 conversion, copper oxide, single crystal catalysts, photo-electro-catalytic (PEC) cells

Introduction. The electrocatalytic reduction of CO_2 is a promising decarbonisation strategy to address the ever-increasingly limited availability of resources and satisfy the future societal needs. The main challenges for this reaction are the high overpotentials needed to perform the multi-electron transfer, and the poor Faradaic Efficiency (FE) to valuable carbon products especially at higher current density [1]. Understanding of mass transfer phenomena and charge diffusion under realistic working conditions is a prerequisite for the rational design of electrocatalysts/electrodes leading to high carbon selectivity [2]. The aim of this work is to develop novel gas-diffusion electrodes (GDEs) based on earth-abundant materials to be integrated in new engineered artificial leaf-type devices for the efficient production of solar fuels [3].

Experimental. CuO nanoplatelets were synthesized by a facile hydrothermal approach at 180°C starting from $CuCl_2 \cdot 2H_2O$ using LiOH or NaOH as the precursors. For the preparation of CuS_x-Bi nanocrystals, $BiNO_3$ and S were also added in the reaction bath. The as-prepared electrocatalytic materials were deposited by spray-coating onto carbon-based GDEs and then assembled in a homemade compact electrochemical device for CO_2 conversion tests. The electrodes were fully characterized by XRD and SEM, and by Electrochemical Impedance Spectroscopy (EIS) to evaluate the influence of diffusion phenomena on the electrocatalytic performance.

Results and discussion. The results showed the high activity of these electrodes in CO_2 reduction in near-neutral pH conditions, mainly due to the thin nanoplatelet structure. We observed a different selectivity depending on the precursor used during the preparation, i.e. Na or Li. The catalyst prepared with LiOH was more selective to carbon monoxide (CO), evidencing a FE to CO of 45% (with a current density of 9 mA cm^{-2} at –0.6 V vs. RHE), while using NaOH as the precursor led to a higher FE to formate. The introduction of S and Bi in the catalyst nanoarchitecture (see the resulting structure in the figure) allowed to further increase the selectivity to formate to over 80 % (with a current density of 9 mA cm^{-2} at –1.0 V vs. RHE) and to obtain also the production of C2 products such as oxalic acid. Furthermore, the activity of these catalysts was strongly influenced by the configuration of the electrochemical cell, evidencing the importance of the role of electrode and cell design in determining the performance beyond the properties of the electrocatalytic material itself, at least under reaction conditions relevant to industrial scalability [4]. We used a new engineered compact system designed to minimize energy losses due to overpotential. The integration of this electrochemical cell with a low-cost photovoltaic system is also presented and discussed, paving the way towards the implementation of efficient artificial leaf-type devices for the production of solar fuels.

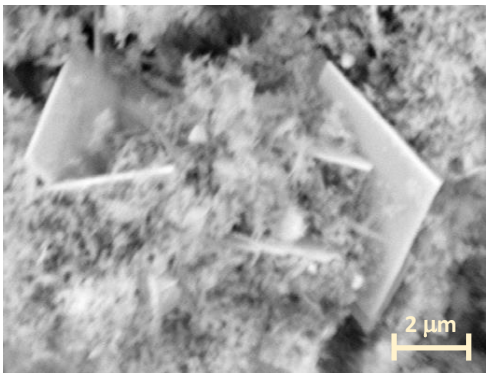

Figure: SEM image of CuS_x-Bi nanocrystals

Acknowledgments

This work is funded by the European Union through the DECADE H2020 project (ID: 862030), which is gratefully acknowledged.

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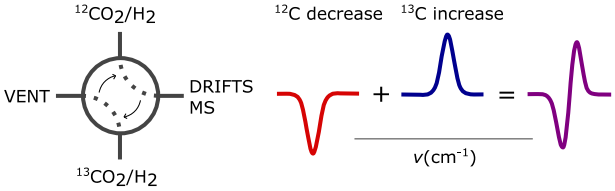
Unraveling the Role of Carbonates on the Reverse Water-Gas Shift Reaction over solid Mn catalyst

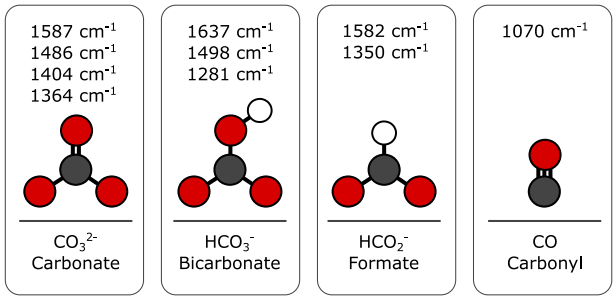
M. Kock[1*], J.J. Mielby[1], S. Kegnæs[1]

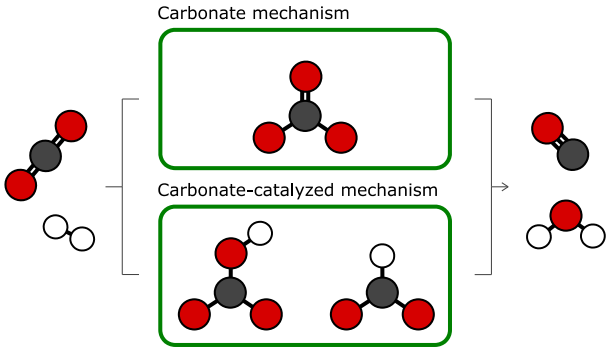
[1]*Technical University of Denmark, Kgs. Lyngby, 2800, Denmark*
*mikola@kemi.dtu.dk

Keywords: RWGS, ME-PSD, Operando FTIR, CO_2 hydrogenation, mechanistic study, catalysts

Introduction. Catalytic reduction of CO_2 to CO via the Reverse Water-gas Shift reaction is attracting renewed interest in producing more sustainable syngas. Many catalysts have been researched, but often suffer from price and selectivity.[1]
To understand and design a good catalyst and improve it, the reaction mechanism is of great interest to understand. Two of the main reaction mechanisms have been proposed, which are a carbonate mechanism and a carbonate-catalyzed mechanism. Which of these mechanisms is often controlled by the H_2 dissociation – which can either be homolytic or heterolytic dissociation.[2]
In this work, we present a novel, active and selective catalyst consisting of supported Mn – and we dramatically improve the catalyst by promoting it. Furthermore, we explore the reaction mechanisms hereof with various infrared spectroscopy.







Experimental/methodology. The catalysts have been tested in a flow reactor equipped with a water condenser and an NDIR detector, which is tuned for CH_4, CO, and CO_2.
The operando IR studies were performed in a Nicolet iS50 FTIR spectrometer equipped with a Harrick Praying Mantis Cell with an on-line mass spectrometer by Pfieffer Vacuum OmniStar.

Results and discussion. The un-promoted catalysts have shown a conversion of 37% at 1 bar, 650°C with a GHSV of 90.000 in H_2:CO_2 ratio of 3:1. Furthermore, we did show that by promoting the catalyst, there was a 44% increase in activity compared to the intrinsic activity. Interestingly, the addition of promoters has surprisingly increased activation energy significantly. Therefore, analyzing the reaction mechanism with different operando spectroscopy is of interest. It was clearly determined that it was mainly carbonate species on all the catalyst's surfaces. However, coupling with modulation excitation-phase sensitive detection (ME-PSD) showed that short-lived and active species at the Mn-supported catalysts were carbonates. However, the short-lived and active species on the surface of the promoted catalyst were only bicarbonates and formates.[3] This signified that the reaction undergoes two different mechanisms dependent on whether the sample is promoted or not.

Acknowledgments
This work was supported by the Independent Research Fund Denmark (DFF) under the Green Transition Program. Furthermore, thanks to Topsoe A/S for their support.

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MXene-based catalysts for CO_2 hydrogenation

Y. Yan[1], L. Loupias[2], S. Célérier[2], F. Morfin[1], L. Piccolo[1*]

[1]*IRCELYON, University of Lyon, France*
[2]*IC2MP, University of Poitiers, France*
[*]*laurent.piccolo@ircelyon.univ-lyon1.fr*

Keywords: MXenes, $Ti_3C_2T_x$, $Mo_2Ti_2C_3T_x$, single-atom catalysts, CO_2 hydrogenation, reverse water-gas shift.

Introduction. MXenes are recently discovered 2D carbides, nitrides, or carbonitrides [1]. Depending on their composition, they exhibit intrinsic catalytic properties or can be synergistically promoted with metal nanoparticles or single atoms. Unlike for electro- and photocatalysis, thermal catalysis on MXenes has been little investigated so far. Herein, through a systematic study of $Ti_3C_2T_x$ ("MX") and $Mo_2Ti_2C_3T_x$ ("MoMX") MXenes, as-prepared or loaded with ultradispersed metals, trends connecting the MXene surface state, metal resistance to sintering, and catalytic properties in CO_2 hydrogenation are established.

Experimental/methodology. $Ti_3C_2T_x$ and $Mo_2Ti_2C_3T_x$ were obtained from the respective Ti_3AlC_2 and $Mo_2Ti_2AlC_3$ MAX phases by LiF/HCl and HF etching, respectively [2]. After their delamination in water (plus an intercalation step in TBAOH for $Mo_2Ti_2C_3T_x$), Pt, Pd, Cu and Co were deposited onto the MXenes by incipient wetness impregnation. The samples were then drop casted on silica to avoid restacking (Figure 1, right), pretreated under H_2 flow up to 450 °C, and evaluated in a flow-fixed bed reactor at a total reactant pressure of 30 bar (H_2:CO_2 = 3:1). Pre- and post-reaction characterizations involved XRD, XPS, TGA, SEM, and STEM techniques.

Results and discussion. Unlike $Ti_3C_2T_x$, bare $Mo_2Ti_2C_3T_x$ reveals a high activity for the reverse water-gas shift reaction in the 250-350 °C range (Figure 1, top). Furthermore, for both systems, Pt addition at low loading (<1 wt%) enhances the activity and the CO selectivity. In contrast, Pd, Cu and Co negligibly affect the performance of $Mo_2Ti_2C_3T_x$. Together with the metal identity controlling the H_2 activation rate, the superior promoting effect of Pt is ascribed to the greater propensity of this metal to atomically and stably anchor at the MXene surface.

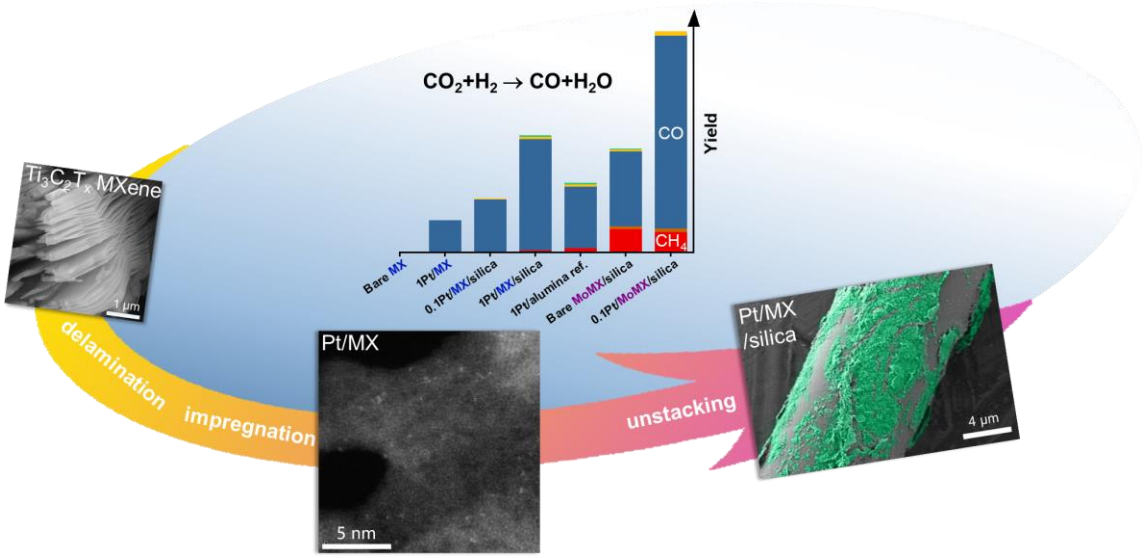

Figure 1. Main steps in the elaboration of Pt/MXene single-atom catalysts and their conditioning for gas-phase catalysis evaluation. CO_2 hydrogenation yields at 275 °C for $Ti_3C_2T_x$ (MX) and $Mo_2Ti_2C_3T_x$ (MoMX)-based catalysts. Blue, red, orange, yellow and green colors correspond to carbon carbon monoxide, methane, higher alkanes, methanol, and dimethyl ether, respectively.

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Competition between reverse water gas shift reaction and methanol synthesis from CO_2: Influence of copper particle size

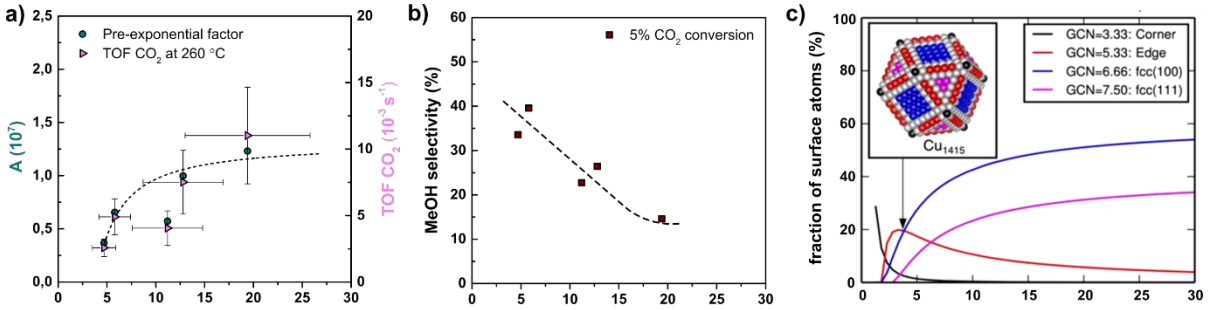
Laura Barberis[1], Amir H. Hakimioun[2], Philipp N. Plessow, Nienke K. Visser, Joseph A. Stewart[3], Bart D VandeGehuchte, Felix Studt[2] and Petra E. de Jongh[1]

[1] *1 Materials Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht (The Netherlands)*
[2] *Institute of Catalysis Research and Technology and Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen (Germany)*
[3] *TotalEnergies One Tech Belgium, B-7181 Seneffe (Belgium)*
[*] *Corresponding Author: p.e.dejongh@uu.nl*

Keywords: CO_2 hydrogenation particle size effects, copper nanoparticles, methanol synthesis

Introduction. Converting CO_2 and renewable H_2 into fuels and chemicals is a promising approach to replace fossil resources. Three factors make CO_2 hydrogenation to methanol more challenging than conventional methanol synthesis: less favourable thermodynamics, a lower catalyst stability due to the less reducing conditions, and the possiblity of forming CO instead via the reverse water-gas shift reaction. In this study we investigated the particle size effects for CO_2 hydrogenation to methanol, by a combination of experimental and computational methods.

Experimental. Size-controlled Cu nanoparticles (4-20 nm) were prepared by incipient wetness impregnation of graphitic carbon supports. The rather inert carbon support is crucial to separate size effects from for instance metal-support interaction. The MeOH synthesis performance was tested in a parallel multireactor set-up (Avantium Flowrence) under 40 bar (g) pressure and at 200-260 °C.



Results. The catalysts showed a good stability and preservation of the size of the Cu nanoparticles during testing, suitable to fundamentally study the effect of particle size on activity and selectivity. Clear particle size effects were observed. The intrinsic activity (Turn-Over-Frequency or TOF, **frame a**) increased approximately 3-fold when increasing the Cu particle size from 4 to 12 nm. Also the selectivity to either MeOH or CO was a clear function of particle size (**frame b)**. Two distinctly different, yet size independent, activation energies were found for MeOH and for CO production (averaging 63±7 kJ mol^{-1} and 118±6 kJ mol^{-1}, respectively). Hence the size dependence was ascribed to a decrease in the fraction of active sites suitable for CO formation with decreasing particle size. Theoretical models and DFT calculations (**frame c)** showed that the origin of the particle size effect is most likely related to the differences in formate coverage for different Cu facets whose abundancy depends on particle size. Hence, the CO_2 hydrogenation reaction is intrinsically sensitive to the Cu particle size.

Relevance : Understanding the active sites and reaction mechanism for CO_2 hydrogenation is crucial to develop effective new catalysts for the production of circular fuels and chemicals .

Reference : L. Barberis et al, Nanoscale 14 (2022), 13551.

Tale of Hot Electrons of Black Gold as Catalyst for Storing Solar Energy into Carbon Dioxide

Rishi Verma and Vivek Polshettiwar*

Department of Chemical Sciences, Tata Institute of Fundamental Research (TIFR), Mumbai, India.
Email: vivekpol@tifr.res.in, Web: www.nanocat.co.in

Keywords: Black gold, plasmonic, photocatalysis, CO2, nanomaterials

Capture and then conversion of CO_2 to valuable chemicals and fuels are the best ways to tackle climate change. We discovered a new nanosilica, Dendritic Fibrous Nano-Silica (DFNS),[1,2] which is now being used by more than 150 groups worldwide for various applications.[1,2] Our group reported several applications of DFNS for catalysis and CO_2 capture-conversions, such as Black Gold[3], Defective Nanosilica[4], Solid Acids[5], Lithium Silicates Nanosheets[6] and Magnesium[7] to combat climate change.

In this talk, I will discuss one of our recent discoveries for solar energy harvesting and CO_2 utilization, using the concept of *"Black Gold as an Artificial Tree".* We transformed yellow gold into black gold by changing the size and gaps between gold nanoparticles supported on nanosilica spheres (due to plasmonic coupling). Black gold harvest board band light of the solar spectrum, the entire visible region, as well as in the near-infrared region. Using black gold, we have now designed and synthesized nickel-laden dendritic plasmonic colloidosomes of Au (black gold-Ni). The photocatalytic CO_2 hydrogenation and organic transformations (hydrogenation, dehydrochlorination etc.), activities of the black gold-Ni increased dramatically to the extent that measurable photoactivity was only observed with the black gold-Ni catalyst, with a very high photocatalytic CO production rate (2464 ± 40 $mmol g_{Ni}^{-1} h^{-1}$) and 95 % selectivity. The catalyst was stable for at least 100 h. Linear dependence of CO production rate on light intensity indicated the non-thermal hot-electron mediated CO_2 reduction. Ultrafast transient absorption spectroscopy studies indicated in-direct hot electron transfer from the black Au to the Ni in less than 100 fs, corroborated by a reduction in Au-plasmon electron-phonon lifetime and a bleach signal associated with Ni d-band filling. Operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) showed that CO_2 hydrogenation took place by direct dissociation path via linearly bonded Ni-CO intermediates.

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CO_2 activation on TiO_2 supported Pt with visible light

M. Huuhtanen[1*], S. Berg[1], M. Mohl[2], A. Popov[3], M. Kärkkäinen[1], A. Dombovari[2], T. Laitinen[1], A. Bykov[3], K. Kordas[2], G. Johansson[4], D. Hedman[4,5], and J. A. Larsson[4]

[1] University of Oulu, Environmental and Chemical Engineering, Oulu, Finland
[2] University of Oulu, Microelectronics Research Unit, Oulu, Finland
[3] University of Oulu, Optoelectronics and Measurement Techniques Research Unit, Oulu, Finland
[4] Luleå University pof Technology, Applied Physics, Division of Materials Science, Department of Engineering Sciences and Mathematics, Luleå, Sweden
[5] Center for Multidimensional Carbon Materials, Institute for Basic Science (IBS), Ulsan, South Korea
** corresponding author: mika.huuhtanen@oulu.fi*

Keywords: CO_2 activation, plasmon, visible light, DRIFTS, Raman, XPS, environmental catalysis

Introduction. To date, highly efficient and selective catalytic reduction of CO_2 represents one of the greatest challenges in the fields of environmental science and energy technology. One major goal, we all driven by, is to convert this chemically inert molecule into useful fuels or chemicals such as methane, formic acid, methanol, or carbon monoxide, e.g. by thermal, electrochemical, and photochemical routes thus alleviating the adverse effects of CO_2 present in the atmosphere.

Experimental/methodology. In this work, visible light (λ=400-500 nm) assisted conversion of CO_2 on Pt and Pd catalysts supported on pristine and N-doped TiO2 anatase nanoparticles is studied using diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) measurements. The micro and crystal structure of the catalysts are analyzed by transmission electron microscopy, physisorption (BET-BJH), Raman spectroscopy and X-ray diffraction. The chemical composition was assessed by X-ray photoelectron spectroscopy. The binding energies of the products on the co-catalysts were calculated by density functional theory (DFT).

Results and discussion. Based on the DRIFTS, on the surface of Pd/TiO_2 minor adsorption of CO_2 in the form of carbonates is found, whereas clear formation of CO is visible apart from carbonates on Pt/TiO_2. XPS results indicate that the Pt as a co-catalyst is mostly in metallic form but Pd is partly oxidized.

The calculations show that the formed carbonates are chemically bound on both PdO (2.0 eV) and Pt (3.1 eV) but CO forms a stable adsorbate only on Pt (1.7 eV), which is in excellent agreement with the DRIFTS measurements.

The results indicate that there is a possible route of CO_2 activation on TiO_2 based catalysts using visible light, which suggest that surface plasmons of the co-catalyst metals may indeed contribute to the chemical reactions.

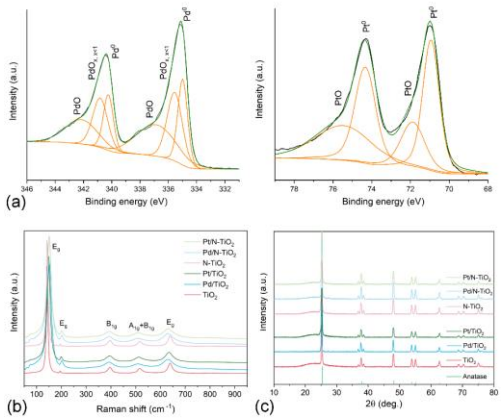

Figure. (a) XPS of the Pd and Pt oxidation states and (b) Raman spectra, and (c) XRD patterns of Pd and Pt decorated pristine and N-doped TiO_2 nanoparticles.

Immobilized Ni particles over hydrotalcite support for CO_2 methanation reaction: On the nature of the active species and the kinetic aspects

Z. Boukha[1], U. De La Torre[1], J.R. González-Velasco[1*]

[1]*Chemical Engineering Department, Science and Technology Faculty*
University of the Basque Country, PO BOX 644, E-48080 Bilbao
[*]*juanra.gonzalezvelasco@ehu.es*

Keywords: CO_2 methanation, Ni/Hydrotalcite, kinetic study, formate pathway

Introduction

CO_2 methanation reaction has attracted a renewed interest since it has been regarded as promising alternative for reducing the global CO_2 emissions, using renewable hydrogen[1]. Recent reports showed that hydrotalcite (HT) supported Ni catalysts exhibited an excellent performance in CO_2 methanation reaction, outperforming those based on traditional supports[2]. The present study deals with the analysis of the effect of Ni loading on the physico-chemical properties and the performance of Ni/HT catalysts. Moreover, a kinetic study has been performed over the optimal formulation to identify the most prevalent mechanism pathway.

Experimental/methodology

A commercial hydrotalcite (3:1 Mg:Al molar ratio; Sigma-Aldrich) was first pretreated at 600 °C for 3 h (5 °C/min) in air. Then, it was impregnated with different amounts of nickel(II) acetylacetone (98 wt.%; Sigma Aldrich) in order to prepare Ni/HT catalysts with 5-30 wt.% Ni loadings. The resulting samples were calcined in air at 500 °C for 4 hours (5 °C/min) and subsequently reduced at 800 °C (5 °C/min) for 2 h in 20% H_2/He. All catalysts were characterized by ICP-AES, XRD, N_2 adsorption-desorption, H_2-TPR, CO_2-TPD, XPS and HAADF-X EDS microscopy. All catalysts were pelletized, crushed and sieved to obtain a 160–250 µm size fraction to avoid transporting effects. Reactions were performed in the 200-500 °C range feeding a 4:1 H_2:CO_2 ratio, balanced with He for a total flow of 125 $cm^3\ min^{-1}$ and a WHSV of 30,000 $cm^3\ g^{-1}\ h^{-1}$.

Results and discussion

Figure 1a shows the light-off curves for all activated Ni/HT samples in the CO_2 methanation reaction. It can be observed that the catalysts with 15-30 wt.% Ni reach the thermodynamic equilibrium at 400 °C. Interestingly, the samples with 15 and 20 wt.% Ni exhibit a similar and the best catalytic performance among the prepared catalysts. Both samples achieved 50% CO_2 conversion at 325 °C and 95% selectivity towards CH_4. The 15%Ni/HT optimal catalyst was also submitted to 90-hour reaction at 350 °C, where only 2% activity loss was observed. Figure 1b shows ultra-high resolution TEM image of the selected catalyst, which allowed measuring Ni dispersion on the catalyst by particle counting, while EDX analysis showed the distribution of the different elements present at the catalyst surface. Finally, the kinetic study performed in the 270-300 °C temperature range shed light on the prevalence of the formate pathway for the description of the reaction mechanism.

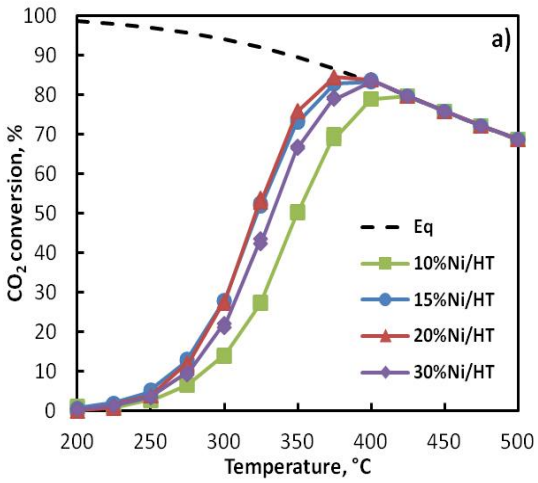

Figure 1. Light-off curves for CO_2 methanation over Ni/HT catalysts and b) TEM image of 15%Ni/HT sample.

Acknowledgments

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Light-assisted CO_2 hydrogenation reactions: mechanistic investigation and catalyst engineering

Binggiao Xie[1*], Tze Hao Tan,[1] Roong Jien Wong[1], Jason Scott,[1] and Rose Amal[1*]

[1]*School of Chemical Engineering, The University of New South Wales (UNSW), Kensington, New South Wales 2052, Australia*

[*]*xiebinggiao@hotmail.com / r.amal@unsw.edu.au*

Keywords: Photo-activation, CO_2 hydrogenation, operando DRIFTS, photothermal catalysis

Introduction. Recently, light-induced activations have been successfully employed to improve the performance of heterogeneous catalysis[1]. However, the mechanism underlining potential interplay between electron excitations and surface chemical processes remains elusive. Herein, we demonstrate, with two conventional CO_2 hydrogenation reaction systems, the importance of probing surface chemistry information for these light-assisted heterogeneous catalytic reactions. We also demonstrate that the catalyst engineering plays an important role in accessing and promoting light-assisted activation.

Experimental/methodology. Photothermal CO_2 hydrogenation experiments were performed using either a Harrick flow reactor system at varying pressures (1-21 bar, for methanol synthesis over $Cu/ZnO/Al_2O_3$ (CZA)) or plug flow reactor system at atmospheric pressure (for CO_2 methanation over $NiO_x/La_2O_3@TiO_2$ (NLT)). Light-triggered surface reactions/variations were studied *via* X-ray spectroscopies and *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Steady-State Isotopic Kinetic Analysis coupled with Diffuse Reflectance Infrared Fourier Transform Spectroscopy (hereby referred to as SSITKA-DRIFTS) was employed to isolate the role of light on promoting rate-determining intermediate steps.

Results and discussion. It is shown in Figure 1A and C that light can improve CO_2 hydrogenation activity over both CZA and NLT. By probing the surface to explore light-triggered surface reactions via X-ray spectroscopies and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), it indicates that electrons originating from the zinc oxide excitation and copper plasmonic excitation serve to activate surface adsorbates, catalysing key elementary processes (namely formate conversion and hydrogen molecule activation), thus providing one explanation for the observed photothermal activity over CZA (Figure 1B)[2]. Furthermore, an isotopic-assisted in situ DRIFTS spectroscopic approach has been established to deliver new evidence and insights on the pivotal role of surface adsorbates in the photo-assisted CO_2 methanation reaction at mild operating temperatures. Specifically, experimental observations reveal that photo-activation of the surface formate intermediate is responsible for an eightfold photo-enhancement on NLT catalyst (Figure 1D)[3]. Further studies show that photothermal activity can be enhanced via effective catalyst engineering strategies [4].

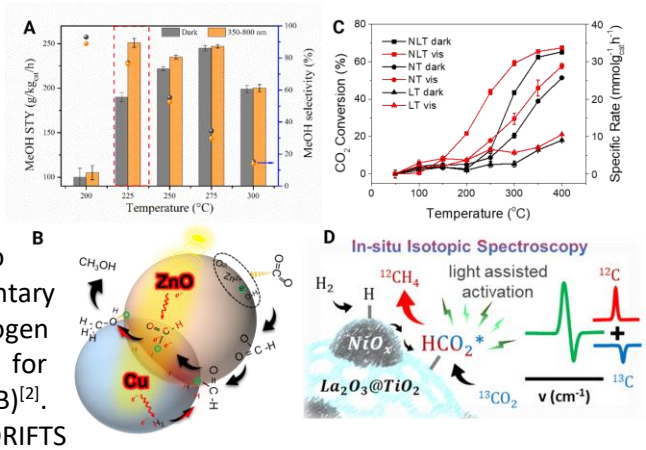

Figure 1. A) methanol space time yield and selectivity under dark and light condition (350-800 nm) over CZA; B) Illustration of synergistic photo-activation over CZA; C) CO2 methanation over NLT; D) Illustration of in-situ isotopic spectroscopy for studying light-assisted intermediate activation over NLT.

Acknowledgement

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CO_2 utilization for on-purpose ethylene production via ethane dehydrogenation over highly selective iron oxide sites

Maria Tasioula[1], Emmanuelle de Clermont Gallerande[2], Anastasia Christodoulou[1], Alessandro Longo[2, 3*], Stavros A. Theofanidis[1,4*], Angeliki A. Lemonidou[1,5]

[1]Department of Chemical Engineering, Aristotle University of Thessaloniki, University Campus, 54124 Thessaloniki, Greece; [2]European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France; [3]Istituto per lo Studio dei Materiali Nanostrutturati (ISMN)-CNR, UOS Palermo, Via Ugo La Malfa, 153, 90146 Palermo, Italy; [4]AristEng S.à r.l., 77, Rue de Merl, L-2146, Luxembourg City, Luxembourg; [5]Chemical Process & Energy Resource Institute, CPERI/CERTH, 57001 Thermi, Thessaloniki, Greece

** Corresponding authors: stavros.theofanidis@aristeng.lu and alessandro.longo@esrf.fr*

Keywords: CO_2 utilization, ethylene production, ethane dehydrogenation, active sites

Introduction

Ethylene is one of the most important commodities in the chemical industry. The abundance of the stranded gas reserves along with the so-called "shale gas revolution" have revitalized the research interest for on-purpose ethylene production, through ethane utilization [1]. CO_2 can act as a mild oxidant for ethane dehydrogenation, shifting the reaction equilibrium, via H_2 consumption through the Reverse Water-Gas Shift reaction. Iron oxide – based catalysts were reported to preserve the C-C bonds and thus resulting in C_2H_4 production [2]. In the present work, the nature of active sites of iron oxide-based catalysts is investigated.

Experimental/methodology

Support and catalyst preparation: For the two-step synthesis, 10wt%NiO-MgO-ZrO_2 support (named "10NiMgZr") was prepared using a sol-gel auto-combustion method [3]. 5wt% Fe catalysts were prepared by wetness impregnation of the Fe precursor on the 10NiMgZr support. The catalysts were calcinated at 600°C for 3 hours and at 700°C for 5 hours respectively, under continuous air flow and then labeled as Fe-600 (3h) and Fe-700 (5h). One step synthesis was implemented for the preparation of 5wt%Fe-10wt%NiO-MgO-ZrO_2 catalyst, using a sol-gel auto-combustion method. The catalyst was calcined at 800°C for 4h, under continuous air flow. Catalyst characterization: Advanced characterizations techniques were performed at BM23 and ID20 beamlines of European Synchrotron Radiation Facility (ESRF). Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near-Edge Structure (XANES) were conducted at Fe and Ni *K* edges, while X-ray Raman Scattering spectroscopy (XRS) at O *K* and Mg $L_{2,3}$ edges.

Results and discussion

Activity tests were performed for all the catalysts during CO_2 – EDH co-feeding at 650°C, P =101.3 kPa and molar feed ratio of CO_2/C_2H_6 =1. At the reactor outlet, the main detected product was C_2H_4, along with CO, CH_4 and minor amounts of H_2 and H_2O. As it is highlighted in Figure 1, Fe-700 (5h) achieved the best performance, reaching 90% selectivity towards ethylene production, at a conversion level of 23.3%, resulting to a maximum ethylene yield of 21%. The enhanced performance of Fe-700(5h) catalyst was attributed to the incorporation of Fe into the support lattice, under reaction conditions, causing a modification of the Mg geometry, as it was proven by XRS data at Mg $L_{2,3}$ edge and consequently of electronic environment of lattice oxygen. FT-IR spectroscopy combined with in situ adsorption of pyridine showed a four-fold increase of acidity for Fe-700(5h) compared to the Fe-600(3h) catalyst, which might explain the increased selectivity towards ethylene.

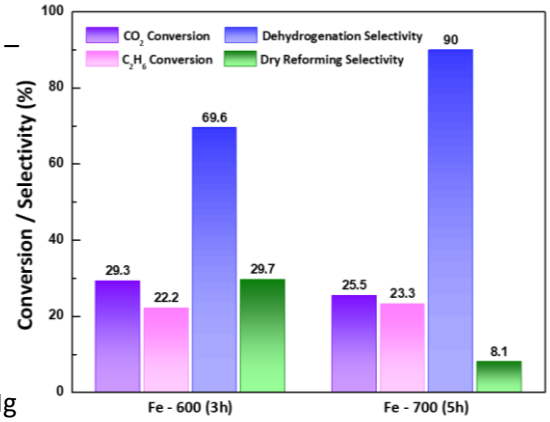

Figure 1: C_2H_6 and CO_2 conversions (%) along with selectivities (%) towards C_2H_4 and syngas production for the investigated catalysts at 650°C. W_{cat}/F^0 =10.8 kg_{cat}·s·mol^{-1}, TOS = 6h.

Acknowledgments

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Application of Molybdenum Carbide Catalysts for the CO_2-assisted Oxidative Dehydrogenation of Ethane

W. Marquart, M. Claeys and N. Fischer*

*Catalysis Institute and DSI-NRF Centre of Excellence in Catalysis c*change, University of Cape Town, Cape Town, South Africa*
**nico.fischer@uct.ac.za*

Keywords: oxidative dehydrogenation, CO_2, ethane, ethylene, molybdenum carbide

Introduction. Mo_2C has shown to be a promising catalyst for CO_2-activating processes such as CO_2 hydrogenation [1], reverse water-gas-shift (RWGS) [2], methane dry-reforming [3] and the oxidative dehydrogenation of short alkanes with CO_2 (CO_2-ODH) [4, 5]. This study focuses on CO_2-ODH, a process that could play a significant role in the synthesis of ethylene through parallel CO_2 activation. At present, the continuously rising demand for light olefins is met predominantly via catalytic/thermal dehydrogenation processes of alkanes at temperatures of up to 900 °C. Under these harsh process conditions high CO_2 emissions, competing side reactions and catalyst deactivation via coking are major challenges. Co-feeding an oxidant, such as CO_2, significantly decreases the reaction temperature [6].
An effective CO_2-ODH Mo_2C-based catalyst is required to activate CO_2, forming oxygen surface species, and simultaneously activate the C-H bond of the alkane. Previously, supported Mo_2C catalysts show great initial activity and high alkene selectivity [4] but are challenged by a poor catalyst stability, caused by oxidation of the carbide phase or carbon deposition [5, 7].
Experimental/methodology. In the present study, the deactivation mechanism of molybdenum carbide catalysts under CO_2-ODH condtions is investigated via modification of the carbide catalyst as well as the reaction conditions. The Mo_2C nanoparticles are supported on various metal oxide support materials. The effect of the various supports on the chemical and structural properties were investigated using temperature progreammed desorption and activation experiments. The *in situ* activated catalysts were then exposed to a variety of CO_2-ODH conditions, in the presence and absence of H_2 co-feeding.
Results and discussion. Our results show that Mo_2C can readily activate CO_2, even in the absence of a reducing co-reactant. The addition of reducible metal oxides as a support material, attempting to achieve a tandem catalyst system balancing CO_2 and ethane activation, did not reduce the degree of oxidation sufficiently. Upon co-feeding different concentrations of H_2, the oxidation of the catalyst can be prevented, keeping ethylene formation routes intact and results in increased stability. A balance between CO_2-ODH and RWGS ensures the removal of oxygen surface species.

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Inverse Zn^{2+}/CuO_x for methanol selective CO_2 hydrogenation

Xinwei Ye[1], Kang Cheng[2], Florian Merier[1], Bert M. Weckhuysen[1*]

[1]*Debye Institute for Nanomaterials Science and Institute for Sustainable and Circular Chemistry, Utrecht University, Universiteitsweg 99, 3594 CG Utrecht, the Netherlands*
[2]*Xiamen University, Xiamen, China*
[*]*B.M.Weckhuysen@uu.nl*

Introduction. Extensive CO_2 emissions into the atmosphere overload the carbon cycle in our ecosystem, which has triggered intensive investigations towards CO_2 capture and valorization processes.[1] Zinc oxide supported copper catalysts are known for CO_2 hydrogenation to methanol, however, high methanol selectivity is still hard to achieved due to the formation of CO as byproduct.[2,3] In this context, conversion of CO_2 to methanol is particularly attractive over the catalyst with a confined inverse Zn^{2+}/CuO_x active center (Cu-ZnZEO), i.e. finely dispersed CuO_x clusters confined withih a Zn-doped zeolite. Following the dynamics of reaction intermediates as well as the evolution of the Cu/Zn speciation at working conditions provide insights into the active structures and reaction pathways for high methanol selectivity.

Experimental. A series of Cu-ZnZEO catalysts with different Cu/Zn ratios were synthesized. Catalytic CO_2 hydrogenation reaction was carried at 220 °C, and 10 bar in a fixed bed reactor. The solid catalysts were characterized with X-ray Diffraction (XRD), UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS) and pyridine-/CO-adsorbed Fourier Transform Infrared (FTIR) spectroscopy, and the reaction pathway was studied via in-situ FT-IR spectroscopy and X-ray Absorption Spectroscopy (XAS).

Results and discussion. The monodispersed nature of Zn^{2+} in Cu-ZnZEO was proved by XRD, UV-Vis DRS and CO-adsorbed FT-IR spectroscopy. The CO-adsorbed FT-IR spectroscopy showed Zn ion stayed isolated even after a reduction process,. A higher Space-time Yield (STY) of desired methanol per Cu was obtained in Cu-ZnZEO with the lowest Cu loading, but the STY of CO was unchanged in all the tested Cu-ZnZEO materials. During catalytic CO_2 hydrogenation, Cu^{2+} was partially reduced into Cu^{+} and Zn^{2+} was maintained. Adsorbed CO and bridged formate were observed, and methanol yield is found related to the CO adsorbed on isolated Cu^{+}, indicating the methanol is selectively produced by the Reverse Water Gas Shift (RWGS) and CO hydrogenation pathway. The CO production is related to the framework of zincosilicate. The *HCOO adsorbed on $Zn^{\delta+}$, however, cannot further convert to methanol due to the high energy barrier in the subsequent hydrogenation steps. However, because the relatively low stability of zincosilicate at the reaction condition, the Cu^{+}-O-$Zn^{\delta+}$ interface gradually disappeared during the CO_2 hydrogenation reaction, resulting in the phase separation of Cu and Zn and thus a continuous decrease of methanol yield. Structure dynamics from given by in-situ XAS results will be presented in the lecture.

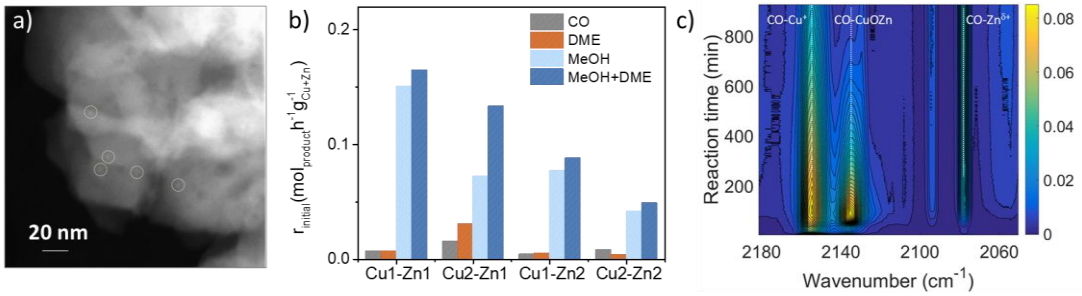

Figure 1. a) Transmission Electron Microscopy (TEM) image b) Initial reaction rate in first 1.5 h, and c) Contour plot of the CO vibrational region at catalytic CO_2 hydrogenation conditions of Cu-ZnZEO.

Acknowledgments

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Metal-organic framework-based catalysts for CO_2 hydrogenation: Insights from kinetic isotope effect studies

D. Makhmutov[1], Bunyarat Rungtaweevoranit[2], S. Wohlrab[1], U. Armbruster[1], A. M. Abdel-Mageed[1*]

[1]*Leibniz-Institut für Katalyse e. V., Albert-Einstein-Str. 29a, 18059 Rostock, Germany*
[2] *National Nanotechnology Center (NANOTEC), Pathum Thani, Thailand*
[*]*ali.abdelmageed@catalysis.de*

Introduction. CO_2 removal from flue gases or capturing it from the air and subsequent conversion into value-added chemicals may be part of the solution to slowing global warming [1]. Among several approaches, CO_2 hydrogenation to methanol is considered one of the most promising routes for both chemical storage of hydrogen as well as provision of a platform chemical for wide range of chemical transformations. Metal-organic frameworks (MOFs) have attracted great interest in catalysis due to their porous structure and tailorable physicochemical properties [2]. In this work, we report the catalytic performance of Cu clusters supported by UiO-66 MOF in gas-phase CO_2 hydrogenation under high pressure. We focused on screening the product selectivity under different reaction conditions by performing kinetic and kinetic isotope effect measurements (KIE) in CO_2/H_2 and CO_2/D_2 gas mixtures.

Experimental/methodology. Cu clusters were loaded into a Zr-based UiO-66 MOF using a solvothermal method described elsewhere [3]. Catalytic performance was investigated in a stainless steel fixed-bed flow reactor with online GC for product analysis. All measurements and characterizations were performed after reductive treatment at 300 °C. The H/D kinetic isotopic effect was studied by switching from $N_2/CO_2/H_2$ to $N_2/CO_2/D_2$ with ratios of 1:3:9 under steady-state conditions. The freshly prepared Cu_x/UiO-66 catalysts were characterized by a variety of surface and bulk sensitive methods.

Results and discussion. Catalyst tests at 250 °C showed significant changes in the reaction behavior with time-on-stream. First, we observed an initial rapid activation phase in which the highest catalytic activity was reached after 20 hours, and then a decrease until reaching a steady state after about 30 hours on-stream. In correlation with the CO_2 conversion rate, we found an increase in ethanol formation, which also decreased over time with the subsequent decrease in CO_2 conversion. This contrasts with methanol formation, which increased continuously over time (change in selectivity from 15% to about 40%). Temperature variation under steady-state conditions showed that methanol was always the predominant product, with the highest selectivity of 93.4% obtained at 200 °C. No formation of CO was observed at this temperature, but other products such as dimethyl ether were detected in limited amounts (Fig. 1). Methanol and DME showed an inverse kinetic isotope effect between 0.8 and 0.5 depending on temperature in agreement with the literature [4]. Ethanol was not observed in D_2. This indicates a much larger inverse KIE for ethanol, which could be due to a highly limited reaction by a hydrogenation step. These results shall be discussed along with the results of detailed KIE studies and DFT calculations.

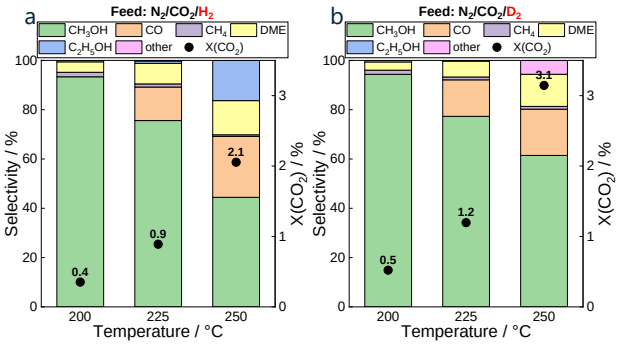

Figure 1. Relationship of product selectivity to reaction temperature: (a) $N_2/CO_2/H_2$ = 1:3:9, (b) $N_2/CO_2/D_2$ = 1:3:9; P = 50 bar, GHSV = 1906 mL·g$^{-1}_{cat}$h^{-1}.

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Effect of In content on In_2O_3/ZrO_2 catalysts for methanol synthesis via CO_2 hydrogenation

Ignacio Tapia[1], Francisco Villagra-Soza[1], Alejandro Karelovic[1], Romel Jiménez[1*]
[1]*Carbon and Catalysis Laboratory (CarboCat), Department of Chemical Engineering, Universidad de Concepción, Chile.*
[*]*romeljimenez@udec.cl*

Keywords: Methanol synthesis, oxygen vacancy, CO_2 hydrogenation, indium oxide

Introduction.

The efficient use of CO_2 as a raw material for the chemical industry is an appreciated topic for mitigating greenhouse gas emissions [1] and to reducing the use of fossil fuels. Among the different routes, hydrogenation to CH_3OH has great projection due to its relevance in the industrial and energy sector, which is hindered by a high CO formation. Within the variety of catalysts, In_2O_3 has showed outstanding selectivity and stability. Additionally, ZrO_2 appears as an interesting support because it creates oxygen vacancy (O_v) in the indium oxide, which are considered the active sites for the reaction [3]. In this work, the performance of Indium supported catalysts at different In/Zr ratios was analyzed to determine the effect of the interaction between In_2O_3 and ZrO_2 and the nature of O_v on the methanol and CO formation rates.

Experimental/methodology.

In_2O_3 catalysts supported on ZrO_2 at different In/Zr molar ratios were prepared by wet impregnation method by varying the amount of $In(NO_3)_3{\cdot}xH_2O$. Two pure In_2O_3 catalysts were synthesized by precipitation (In_2O_3-P) and thermal decomposition (In_2O_3-DT) method. The materials were characterized by XRD, N_2 sorption at 77 K and N_2O-RFC to quantify oxygen vacancies. The catalytic tests were carried out in a fixed bed differential reactor under temperature (220-280ºC) and flow control at 8 bar. The composition of the gases was measured by a gas chromatograph.

Results and discussion.

The ZrO_2-supported In catalysts showed higher space time yield per gram of Indium than the Cu-Zn-Al catalyst per gram of Cu at T>240ºC (Fig. 1a). Moreover, the selectivity toward CH_3OH of the In-based catalysts resulted significantly higher than that observed for Cu-Zn-Al at all conditions studied (Fig. 1b), being less sensitive to the increase of temperature. The decrease in selectivity at higher temperatures is related to the favoring of RWGS, which is particularly pronounced in the Cu-based catalyst, due to its high difference between the activation energies for CO and CH_3OH formation. This results suggest important differences in terms of mechanism and nature of active sites involved between the In-based catalysts (O_v are proposed) and Cu-based catalysts [2]. Fig 1c shows that the density of O_v per gram of indium measured by N_2O-RFC decreases with increasing indium loading, showing higher use of the material. Moreover, the rates of CH_3OH and CO formation per mole of O_v showed different behaviors as a function of In content in the catalyst, indicating a difference in the nature/quality of O_v to form both products. The observed performance of the supported materials, higher activity at lower loading, may be related to the particle distribution as a function of content, which is related to the XRD results on the supported catalysts (17.9 nm for 3:10, 22.4 nm for 5:10 and not measurable for 1:10), suggesting an effect of crystal diameter on the O_v and thus on their activity.

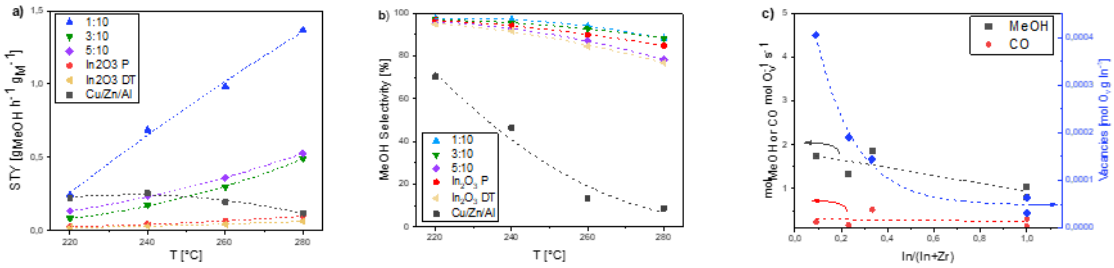

Figure 1: a) Methanol STY per gram of metal (In or Cu) and b) methanol selectivity as a function of temperature. c) Moles of CH_3OH or CO formed per oxygen vacancy and oxygen vacancy per gram of indium as a function of their molar composition. Reaction conditions: P=8 bar and H_2/CO_2=4.

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A spatially-resolved operando FT-IR analysis on Dual Function Materials (DFMs) for CO_2 capture and hydrogenation from flue gases

Alessandro Porta[1], Roberto Matarrese[1], Carlo Giorgio Visconti[1] and Luca Lietti[1]*

[1]*Department of Energy, Politecnico di Milano, Milan, 20156 (Italy)*
** luca.lietti@polimi.it*

Introduction. In order to comply with international agreements on the reduction of CO_2 emissions, a marked increase in the use of renewable energy and carbon capture and utilization technologies is foreseen. In particular, an appealing solution is represented by the combined capture of CO_2 and hydrogenation using green H_2 over Dual Function Materials (DFMs) [1, 2]. The idea is to work under cyclyc conditions to capture CO_2 from a CO_2-containing stream (e.g. combustion flue gases) on the DFM, and then exposing the CO_2-saturated DFM to renewable H_2 to produce CH_4 and regenerate the adsorbent. This is a recently proposed application and the optimal catalyst formulation is still under debate. By combining microreactor experiments and spatially resolved operando FT-IR in this work we provide insights on DFMs performances, reaction mechanism and stability when exposed to different species that are present in combustion flue gases, such as H_2O, O_2 and NO_x.

Experimental/methodology. Al_2O_3-supported DFM were prepared by sequential impregnation of $Ru(NO)(NO_3)_3$ and Na, K or Ba from the corresponding acetate or carbonate salt [3]. The DFMs were then characterized by N_2 physisorption, XRD, SEM-EDX, CO_2 TPD, H_2 TPR, TGA, H_2 and CO chemisorption experiments, in-situ and operando FT-IR spectroscopy. CO_2 capture/reduction cycles were performed at constant temperature in the range 250-400°C. Every cycle is composed by an adsorption phase (1% CO_2/He) and a reduction phase (4% H_2/He), separated by an inert purge. The adsorption phase is progressively enriched with H_2O, O_2 and NO. The cyclic experiment were performed using both a fixed bed quartz microreactor and an operando FT-IR low dead volume cell (#CSX, AABSPEC) allowing for spatial resolution. In both cases the outlet gases were monitored with a mass spectrometer, a FT-IR gas analyzer and a microGC.

Results and discussion. H_2O has an inhibiting effect on the amount of adsorbed CO_2 due to a competitive adsorption effect for the same basic sites. Furthermore, spectroscopic evidence demonstrated that the presence of H_2O causes a change in the nature of the adsorbed species, converting the bidentate carbonates to ionic/bulk carbonates, which are more difficult to reduce and tend to accumulate on the DFM surface. O_2 causes minor losses in the amount of adsorbed CO_2 due to the oxidation of Ru metal sites (which are capable of adsorbing CO in O_2-free conditions) but causes a decrease in the CH_4 formation rate due to the additional step of Ru-oxide reduction, and in some condition may also induce Ru sintering. When NO_x is present in the adsorption feed, it preferentially adsorbs as nitrate onto the SM resulting in a lower CO_2 storage capacity. However, spatially-resolved operando FT-IR indicated that NO_x is adsorbed on the catalyst bed as a moving front (Figure 1), and significant amounts of CO_2 can still be adsorbed in presence of small amount of NO_x by calibrating the duration of the adsorption phase.

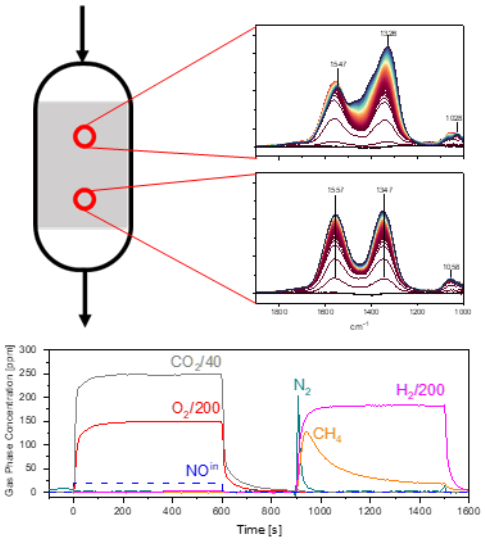

Figure 1. Spatially resolved operando FT-IR during CO_2 capture in the presence of NO_x

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Mechanistic relationship between CO and CO_2 hydrogenation over mono- and bimetallic Ni, Co and NiCo catalysts

Francisco Villagra-Soza[1], Tomás Vergara[1], Sebastián Godoy[1], Alejandro Karelovic[1],Romel Jiménez[1]*

[1] *Carbon and Catalysis Laboratory (CarboCat), Department of Chemical Engineering, Universidad de Concepción, Chile*

romeljimenez@udec.cl

Keywords: CO_2 valorization, CO_2 hydrogenation, Operando-FTIR, SSITKA-DRIFTS, KIE

Introduction.

The increase in atmospheric CO_2 levels has generated negative effects on the climate. Sustainable processes have been promoted to mitigate these effects and reduce the utilization of fossil fuels. The synthesis of clean fuels through the hydrogenation of CO_x to CH_4 shows great projection since it requires moderate reaction conditions and can be easily integrated to existing infrastructure. However, the rational design of active, selective and stable catalysts is mandatory and requires knowing in detail the reaction mechanism. In this work, CO_2 and CO hydrogenation reactions were studied by kinetic, isotopic (KIE, SSITKA-DRIFTS) and Operando-FTIR measurements in order to understand the mechanistic relationship between the reactions.

Experimental/methodology.

Mono and bimetallic 5%wt Ni, Co and Ni-Co supported catalysts were prepared by incipient wet impregnation with varying Co molar composition (Co/(Co+Ni)). The materials were characterized by TEM and XRD. A kinetic and H_2/D_2 kinetic isotope effect (KIE) studies were conducted in a fixed bed differential reactor controlling the temperature, H_2/D_2 and CO_x feeds. Effluent composition was measured with a gas chromatograph. Operando-FTIR analysis were performed in a differential reaction cell, with a self-supported catalyst wafer. SSITKA/MS-DRIFTS measurements were executed in a low dead volume differential reaction cell by changing the feed from Ar/$^{13}CO_2$/He/H_2 to $^{12}CO_2$/He/H_2, and the effluents were followed with a mass spectrometer.

Results and discussion.

Characterization of the catalysts confirmed similar dispersion (~20%) of the materials ruling out structural sensitivity effects[1,2] on the measured rates. TOF_{CH4} from CO_2 hydrogenation showed a negative displacement with respect to metal-weighted activity in CO_2 hydrogenation, while from CO showed a slight synergistic effect (Fig1.a). This behavior cannot be explained by the increased of CO* coverage when CO is fed, compared with CO_2, as proposed on Rh[3], since higher TOF_{CH4} in the reaction with CO_2 would be expected for all catalysts; nevertheless, it is only observed on Ni. Furthermore, Operando-FTIR results show that co-feeding CO leads to higher CH_4 formation rates, despite the increase of CO* coverage (Fig 1b,c). The kinetic analysis show apparent reaction orders ~0.5 for TOF_{CH4} with respect to P_{H2} for both reactions, suggesting its participation in the RDS and consistent with the observed inverse KIE (Fig 1,a). Higher $TOF_{ITK-CH4}$ from the CO_2 labeled SSITKA/MS-DRIFTS studies on NiCo (0.145 s^{-1}) than on Ni (0.042 s^{-1}) indicates lower specific reactivity on Ni but a higher density of intermediates was obtained, consistent with IR measurements showing a higher ratio of active multibond CO to CH_4[2]. In addition, a greater shift towards CO weakly adsorbed on NiCo is observed, which explains the different behaviors in CO and CO_2 hydrogenation.

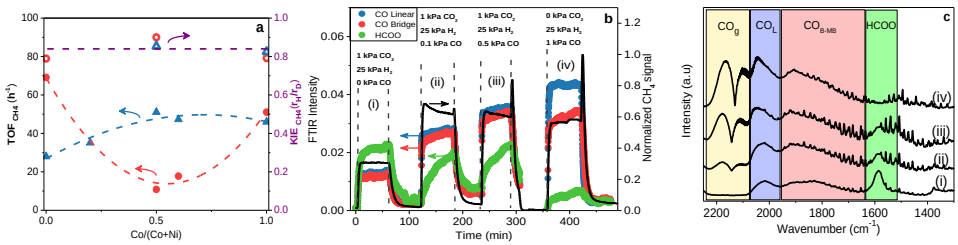

Figure 1. a) TOF (filled symbols) and kinetic isotope effect, KIE (empty symbols) for CH_4 formation in the hydrogenation of CO (▲Δ) and CO_2 (●○) at 1 kPa CO_x-25 kPa H_2 and 280C, as a function of catalyst content. b) In-situ FTIR-MS and c) steady state FTIR for changes from CO_2+H_2+CO to H_2, varying the P_{CO} on the NiCo catalyst at 200°C.

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Optimisation of Cu-CeO_2 catalysts for the CO_2 hydrogenation to MeOH

E. Calì[1,2*], F. Salomone[1], S. Bensaid[1], D. J. Payne[2], F. A. Deorsola[1]

[1] *Department of Applied Science and Technology (DISAT), Polytechnic of Turin, C.so Duca degli Abruzzi 24, 10129 Turin, Italy*

[2] *Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, U.K.*

[*] *Corresponding Author: eleonora.cali@polito.it, e.cali14@imperial.ac.uk*

Keywords: Copper oxide, ceria, exsolution, nanoparticles, methanol, CO_2 hydrogenation

Introduction. With CO_2 emission currently having the highest impact on the greenhouse effect, a sustainable and smart approach to reduce such environmental footprint involves the capture and utilization of the emitted CO_2 as carbon source for fuels and materials, by recycling it and reusing it in a loop. The CO_2 chemical valorisation aims at converting CO_2 into a variety of useful products, such as chemicals and fuels. An example is the catalytic conversion of CO_2 and H_2 into methanol (MeOH), a widely usable component for fuels, plastic, paints, textile chemicals, and a building block for the synthesis of more complex fuels. Although there is also growing interest in the implementation of this research area at industrial level due to its great economic potential, a major challenge related to the process is the low CO_2 conversion, triggered by limited catalyst selectivity and deactivation by active metal nanoparticle (NP) sintering. Recently, it has been proposed that the synergistic effect of copper and ceria in the hydrogenation of CO_2 to methanol influences the activity, selectivity and stability of these Cu-based catalysts [1]. The present study focuses on the development of different Cu-CeO_2 catalysts for the conversion of CO_2 and H_2 into methanol.

Experimental/methodology. Several Cu-CeO_2 binary catalysts were synthetised by employing different synthesis techniques (*i.e.*, wet impregnation (WI), solution combustion synthesis (SCS), and gel-oxalate co-precipitation(OX)) and by varying the Cu/Ce atomic ratio. Moreover, due to the Cu high mobility when infiltrated on oxide surfaces often leading to undesidered thermal agglomeration of Cu NPs at operating conditions, exsolution of Cu NPs from monophasic Cu-doped CeO_2 particles under high-temperature reducing conditions was also investigated. The samples were tested in a fixed-bed reactor under different reaction conditions. To rationalise their catalytic performance, all the samples (calcined and spent) were characterised with several techniques such as ICP-MS, N_2 physisorption, XRD, H_2-TPR, CO_2-TPD, XPS, Raman spectroscopy, SEM, TEM, and STEM-EDX spectroscopy.

Results and discussion. The addition of different amounts of Cu into ceria boosted the catalytic activity of the samples by improving the methanol yield. As illustrated in Figure 1, SCS and OX synthesis techniques lead to smaller particles with an improved interaction between Cu and CeO_2 phases. Characterisation results revealed that the specific surface area increased as the average crystallite size of the two phases diminished, rising the point of contacts between the two phases and, hence, the active sites of the reaction. Finally, the exsolution strategy was employed in order to obtain Cu-metal NPs with a strong anchorage of the NPs to the CeO_2 support and, due to the strain imposed by the NPs at the interface with the support by their unique "socketing" (*i.e.*, anchorage) [2], to maximise the Cu/CeO_2 interaction and stabilise the Cu NPs on the surface of CeO_2.

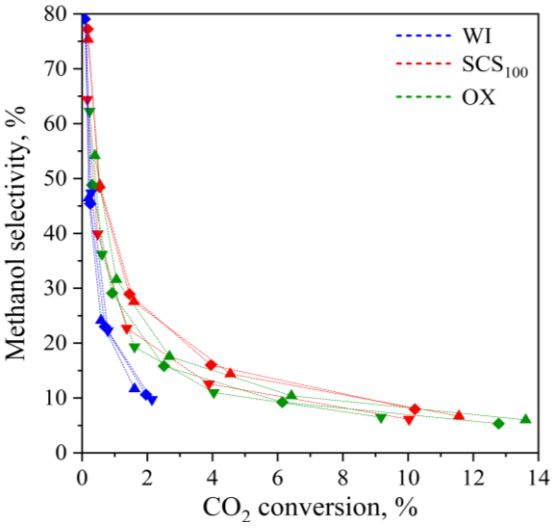

Figure 1. Conversion-selectivity map of the Cu-CeO_2 binary catalysts synthetised with different methods and Cu/Ce ratios (2.5 MPa, 20 NL·g_{cat}^{-1}·h^{-1}, H_2/CO_2 = 3, 200 – 300 °C).

Acknowledgments

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Carbon–ZrO_2 composite as support for Ni-based CO_2 methanation catalyst

Inês F. Quatorze,[1,2] Liliana P. L. Gonçalves,[1,2,3] Yury V. Kolen'ko,[3] M. Fernando R. Pereira,[1,2] O. Salomé G. P. Soares,[1,2,*]

1 LSRE-LCM - Laboratory of Separation and Reaction Engineering, Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr.Roberto Frias, 4200-465, Porto, Portugal

2 ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

3 International Iberian Nanotechnology Laboratory, Avenida Mestre José Veiga, 4715-330 Braga, Portugal

**salome.soares@fe.up.pt*

Keywords: CO_2 methanation, CNT, composites

Introduction. CO_2 methanation ($CO_2 + H_2 \leftrightarrow CH_4 + H_2O$) is of great interest since it is the most energetically advantageous reaction to valorise CO_2 as carbon source, with respect to thermodynamics. Supported nickel-based catalysts are the most commonly used for this reaction, due to their good combination of activity, selectivity and price [1]. However, these materials are susceptible to thermal sintering aggravated by the formation of hot spots during the reaction, leading to deactivation. In this work, the properties of carbon nanotubes and ZrO_2 were combined to obtain a high performing Ni-based CO_2 methanation catalyst. Furthermore, the promotion of the catalyst with Fe was evaluated.

Experimental/methodology. CNT-ZrO_2 composites were prepared with a ball milling procedure, and their composition was optimized. The Ni and NiFe catalysts were prepared by incipient wetness impregnation. The catalysts were characterized and their performance for CO_2 methanation reaction was evaluated in terms of CO_2 conversion (X_{CO2}) and methane selectivity (S_{CH4}).

Results and discussion. The catalytic results of the optimized catalysts are presented in Figure 1. A ratio of CNT:ZrO_2 of 70:30 demonstrated to be optimal to achieve a Ni catalyst with higher X_{CO2} and S_{CH4}, outperforming the Ni on CNT catalyst but not the reference Ni on ZrO_2. Interestingly, the addition of Fe demonstrated to be beneficial, with the 18:2NiFe/CNT-ZrO2 (70:30) catalyst obtaining X_{CO2} = 85.6% and S_{CH4} = 99.9% at T = 370 °C, a result that compares favourably with those reported in the literature and outperforming the Ni on ZrO_2 reference catalyst. The catalyst presented an excellent stability over 70 h of TOS. This systematic study provides evidence that the preparation of carbon:metal-oxides composites could be an interesting approach to achieving high performing catalysts for CO_2 methanation reaction.

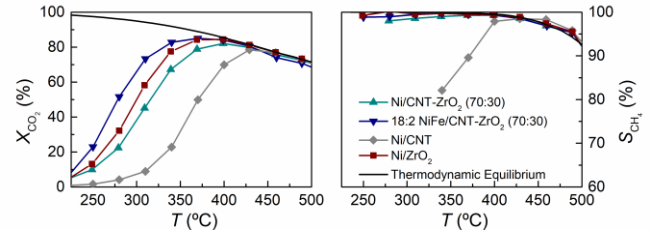

Figure 1. Comparison of the catalytic performance, in terms of X_{CO2} (a) and S_{CH4} (b), at different temperatures.

Acknowledgments

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Monitoring by in situ NAP-XPS of active sites for CO_2 methanation on a Ni/CeO_2 catalyst

S. López-Rodríguez[1], A. Davó-Quiñonero[1], E. Bailón-García[1], D. Lozano-Castelló[1] , I. Villar-García[2], V. Pérez-Dieste[2], J. A. Onrubia-Calvo[3], J. R. González-Velasco[3], A. Bueno-López[1]*

[1]*Inorganic Chemistry Department, University of Alicante, Alicante, Spain*
[2]*ALBA Synchrotron Light Source, Cerdanyola del Vallés, Barcelona, Spain*
[3]*Chemical Engineering Department, University of the Basque Country, UPV/EHU, Bizkaia, Spain*
*agus@ua.es

Keywords: CO_2 methanation, Ceria, Nickel, NAP-XPS, redox active sites

Introduction. Ni/CeO_2 catalysts are very active and selective for total hydrogenation of CO_2 to methane, but the nature of the active sites is still unclear**.** It has been suggested that Ni/CeO_2 catalysts combine two types of active sites working together during CO_2 hydrogenation to methane [1]. Previously, it was postulated that surface oxygen vacancies located at the Ni^{2+}-CeO_2 interface are responsible for the chemisorption and dissociation of CO_2, while reduced Ni^0 sites are more effective for H_2 dissociation. Best Ni/CeO_2 catalysts are those that combine both types of active sites and distribute the nickel available on the catalyst in an optimum proportion between them. Nonetheless, the behaviour and changes suffered by the different active sites of Ni/CeO_2 catalysts under reaction conditions is still unknown. Herein, the surface of a Ni/CeO_2 catalyst has been monitored under CO_2 methanation conditions by Near Ambient Pressure-XPS (NAP-XPS) using synchrotron radiation.

Experimental/methodology. NAP-XPS experiments were performed at the CIRCE beamline at the ALBA Synchrotron Light Source. The catalyst was pretreated in situ and XPS spectra were recorded at different temperatures in steady state under CO_2 methanation conditions.

Results and discussion. It has been concluded that the species involved in the redox processes taking place during the CO_2 methanation mechanism are the Ni^{2+}-CeO_2/ Ni^0 and Ce^{4+}/Ce^{3+} pairs. In addition, a small fraction of nickel is present on the catalyst surface forming NiO and Ni^{2+}-carbonates/hydroxyls (around 20% of the total surface nickel), but these species do not participate in the redox processes of the methanation mechanism. Under CO_2 methanation conditions the H_2 reduction rate of the Ni^{2+}-CeO_2/Ni0 and Ce^{4+}/Ce^{3+} couples is much faster than their CO_2 reoxidation rate (2 times faster, at least, at 300 ºC), but a certain proportion of nickel always remains oxidised under reaction conditions. The high activity of Ni/CeO_2 catalysts for CO_2 methanation is tentatively attributed to the simultaneous presence of Ni^{2+}-CeO_2 and Ni0 active sites where CO_2 and H_2 are expected to be efficiently dissociated, respectively [2].

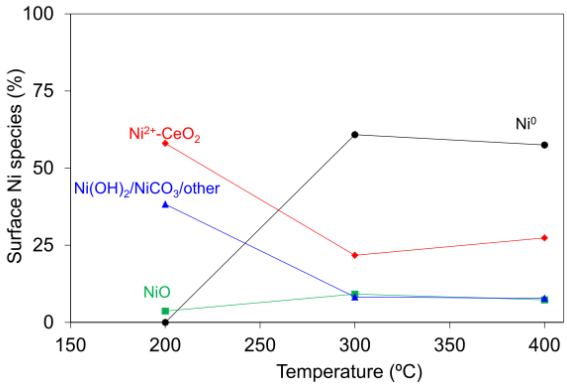

Figure. Evolution of Ni species present on surface during CO_2 methanation experiments in NAP-XPS chamber.

Acknowledgments
ALBA synchrotron, Spain (Proposal number: ID 2020094556). Spanish Ministry of Science and Innovation (PID2019-105960RB-C21, PID2019-105960RB-C22, RYC2021-034791-I, TED2021-129216B-I00, PDC2022-133839-C22), Generalitat Valenciana (CIPROM/2021/74, MFA/2022/036).

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Carbon resistant Ni-Co binary nanoparticles for dry reforming of methane reaction

C. Ciotonea[1], M. Chaghouri[1], M. Marinova[2], P. Simon[3], E. Abi-Aad[1], S. Royer[3], C. Gennequin[1]

[1]Université du Littoral Côte d'Opale, Unité de Chimie Environnementale et Interactions sur le Vivant,UR 4492 Dunkerque, France.
[2] Univ. Lille, CNRS, INRA, Centrale Lille, Univ. Artois, Institut Michel-Eugène Chevreul, Lille, France.
[3]Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181-UCCS-Unité de Catalyse et de Chimie du Solide, Lille, France

Introduction. The alarming concerns on the growth of CO_2 emissions, and its consequences on the global warming, are the trigger to develop and implement CCUS (Carbon Capture, Use and Storage) strategies for the production of highly valuable molecules [1]. On this regard, a very important process is dry reforming of methane (DRM), where CO_2 and CH_4(both a part of the GHG) are reacting for producing syngas (mixture of H_2 and CO). The use of catalyst in DRM reaction is the key to decrease the reaction temperature and to orient the selectivity. Ni and Co are reported to be used in DRM in different catalytic formulation, nevertheless the deactivation by carbon formation or sintering is still obsserved for the spent catalyst. The conception of the catalyst, is focusing in obtaing an accurate distribution of the active species in DRM in order to reach superior performacies and thermaly stable catalyst.

Experimental. We are focusing our attention in this study on the formulation of bimetallic catalyst based on Ni and Co. Our challenge is to control the distribution of the active sites of Ni and Co at the surface of the nanoparticles (NPs) in order to conclude on their impact in the DRM reaction. Thus, we are proposing to prepare catalysts with high loading of 20 wt.% with different ratio of Ni and Co ($Co_xNi_{20-x,}$ where x= 0, 5, 10, 15 and 20). We chose to firstly prepare bimetallic phyllosilicate (PS), as precursor for the production of the bimetallic NPs. Our strategy is to use SBA-15 in order to retain high specific surface and to proceed to a slow deposition precipitation process by using urea [2]. In order to evaluate the material characteristics, investigation was made onto calcined, reduced (H_2-700 °C) and after DRM test, by situ-XRD, N_2 physisorption, TPR, XPS, STEM-EDX-EELS.

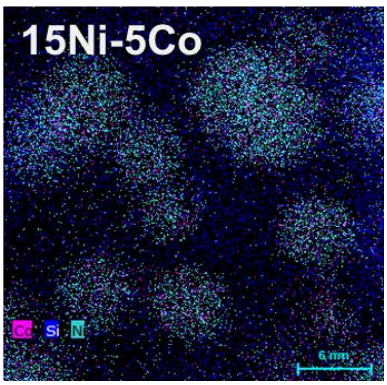

Fig. 1: *STEM-EDX* mapping for *Ni (blue)-Co (fuchsia) within bimetallic NPs*

Results and discussion. For the calcined phases, the XRD and TEM are revealing the presence of phyllosilicates containing both Ni and Co. We can not distinguish on the type of the phyllosilicate or on distribution of Ni/Co onto the layers of the PS. The reduction of the phyllosilicate, is leading to the formation of small NPs of 2 to 6 nm even if we use high metal loading of 20 wt.%. H_2-TPR of NiCo binary materials always occurs below 700 °C, which is > 100 °C lower than for pure 0Ni-20Co sample. The STEM-EDX mapping is showing that the particles rich in Ni have the external layers enriched in Ni, while the core contains both Ni and Co (Fig. 1), although 5Ni-15Co is showing small Co NPs and larger particles with Co rich shells. The materials were tested in the DRM at 700 °C in stoichiometric ratio of CO_2/CH_4, and 20 vol.% in Ar. The results are showing the following order 15Ni-5Co > 10Ni-10Co > 15Co-5Ni, and excellent stabilities during 12h are obtained for 15Ni-5Co due to limited carbon formation and absence of NPs sintering. A stability test for 200 hr of reaction confirmed the excellent stability of this 15Ni-5Co catalyst, with constant conversions, no sintering and limited formation of carbon (TGA-MS analysis < 25 wt.% of carbon accumulated). We associate these results to the spacial distribution of the elemnts, thus, the presence of Ni at the surface of the NPs, while the Co core is busting the conversion at 76% CH_4 and 81% CO_2, leading to a limited formation of coke.

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A Critical View on Direct Syngas to Aromatics over Combined Zinc Oxide on Zirconia and H-ZSM-5 Catalysts

Michael T. Nikolajsen[1*], Niels Christian Schjødt[2], Uffe V. Mentzel[2], Jens Sehested[2], Jakob M. Christensen[1] and Martin Høj[1]

[1]*Department of Chemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby, Denmark*

[2]*Topsoe A/S, Kgs. Lyngby, Denmark*

**mitni@kt.dtu.dk*

Keywords: syngas, aromatics, methanol

Introduction. ZnO supported on zirconia (ZnO/ZrO_2) catalyses methanol synthesis with high selectivity and stability at temperatures >300 °C. When combined with H-ZSM-5 a CO_2 conversion of 14-15 % with an aromatics selectivity of 73-76 % has been reported [1,2]. This work investigates the combination of ZnO/ZrO_2 with ZSM-5 of various acid site densities, for the direct conversion of syngas to aromatics. The mixing ratio and operating conditions were optimized to increase the CO_x conversion and aromatics selectivity. This includes fundamental characterization using BET, ICP and XRD and in-depth characterization using in-situ XAS and DRIFTS.

Experimental/methodology. The ZnO/ZrO_2 was prepared by the incipient wetness impregnation method. H-ZSM-5 materials were obtained from Zeolyst. Activity measurements were conducted in a high-pressure fixed bed flow reactor. DRIFTS was performed in a Harrick Praying Mantis high pressure cell. XAS was performed at Balder, MAX IV (Sweden) and SuperXAS, Swiss Light Source.

Results and discussion. As illustrated in Fig. 1(a) increasing the metal oxide to zeolite ratio did not influence the aromatics selectivity but increased the CO_x conversion and olefin selectivity. The higher metal oxide residence time and the observation that olefin selectivity increased with zeolite deactivation, suggest that olefin hydrogenation and aromatization are competing reactions occurring in the zeolite pores. The higher selectivity to olefins by 4:1 mixing ratio enhanced the potential for forming aromatics by olefin cyclization and hydrogen transfer reactions. This potential was utilized by increasing the acid site densities to a Si/Al ratio of 40 of the ZSM-5, illustrated in Fig 1(b). However, the aromatics selectivity decreased when using a Si/Al ratio of 25, due to an increase in the competing olefin hydrogenation activity. To improve the aromatics selectivity to 33 %, the conditions 320 °C and 10 barg were found optimal, far from the ideal CO_2 conversion conditions at >50 barg and 340 °C. The hydrocarbon pool dual cycle mechanism, states that olefins act as hydrogen acceptors in hydrogen transfer reactions that produce aromatics, which limits the aromatics selectivity that can be achieved [3]. To achieve >70% aromatic selectivity, dehydrogenation reactions must take place, which creates an alternative reaction path for the formation of aromatics. Cyclohexane dehydrogenation equilibrium calculations showed that this is unlikely below 350 °C and at the high hydrogen concentrations in the syngas. In-situ DRIFTS showed adsorption of carbonate species, followed by two-step reduction to formate and methoxy species and desorption of methanol over ZnO/ZrO_2 (Fig. 1(c)).

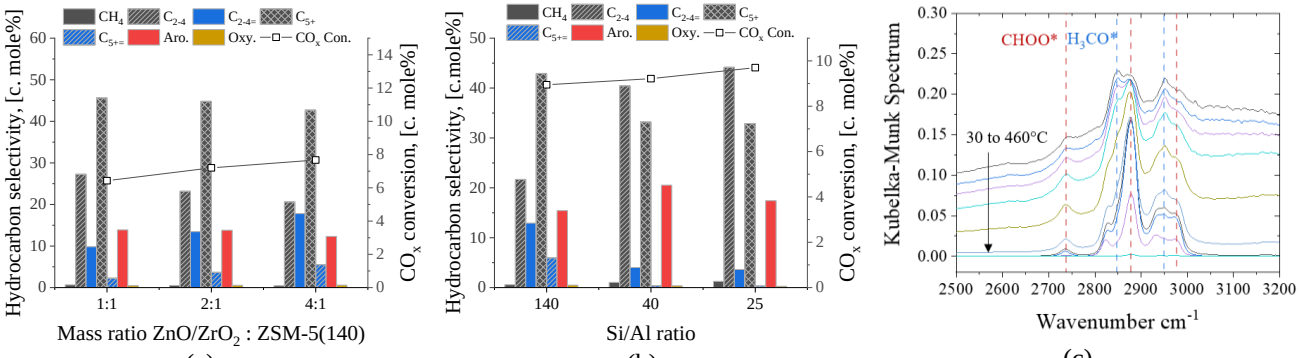

Fig 1. (a) CO_x conversion and product selectivity after 14 hours on stream with ZnO/ZrO_2 and ZSM-5 mixed in different ratios (b) with different Si/Al ratios mixed 4:1. (a,b) Conditions P = 30 bar, $CO_2/CO/H_2/Ar$ = 29/4/64/3, GHSV = 10000 Nml g^{-1} h^{-1}. (c) DRIFTS TPD in He flow after catalyst treatment in syngas.

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CO_2 upgrading via low-temperature RWGS reaction: *operando* mechanistic insights to guide an optimal catalysts design

G. Torres-Sempere[1], L.A. Luque-Álvarez[2], Luis F. Bobadilla, T.R. Reina, L. Pastor-Pérez, J.A. Odriozola.

[1,2]Inorganic Chemistry Department & Material Science Institute, University of Seville-CSIC, *Sevilla, España*
*gtorres1@us.es

Keywords: RWGS, operando DRIFTS, low-temperature, circurlar economy, CO_2 valorisation.

Introduction.

The actual economical and envriomental standing makes necessary the research of new process for the obtation of energy and added-value chemicals from different sources. In this scenario, valorisation of CO_2 via RWGS for the obtention of syngas is an interesting route to achiebe this aim. The main drawback of this reaction is the need of high temperatures (500-700 ^oC) for the obtention of reasonable of catalytic results because CO_2 methanation competes at low temperatures [1]. In order to gain insights of the mechanism of this process to get closer to an active low-temeprature catalyst, Catalytic activity test, operando DRIFTS study and transient experiments have been done over two catalytic systems: Pt/TiO_2 and $PtCs/TiO_2$. Furthermore, the effect of Cs has been also elucidated for this reaction.

Experimental/methodology. Pt/TiO_2 and $PtCs/TiO_2$ catalysts were synthesied by sequential wet impregnation and calcinated at 550 ^oC for 3 h (10 ^oC/min). The catalytic activity test was perfomed over a quartz bed reactor, adding 200 mg of catalyst. Firstly, catalysts were activated at 550 ^oC under H_2/N_2 flow. Then, the reaction was carried out at three different temperatures for 24 h (300, 400 and 500 ^oC) and mataining a H_2/CO_2 ratio of 4/1. Finally, for the Operando DRIFTS measurements, catalysts were activated at 400 ^oC under H_2/N_2 flow and then reaction was carreid out at five different temperatures (150, 200, 250, 300 and 350 ^oC) mataining the H_2/CO_2 ratio of 4/1. Transient experiments were carried out by using pulses of both reactants H_2/Ar and CO_2/Ar, altered during periods of 5 min each one at 250 ^oC.

Results and discussion. Reasonable CO_2 conversiond were achived at low-temepature range. Furthermore, addition of Cs promotes a seletivity of 100% towards CO at 300 and 400 ^oC, and 95% at 500 ^oC (figure 1). The results obtained from Operando DRIFTS measurements indicated that Pt/TiO_2 follow a redox mechanism for the synthesis of CO, while in the $Pt\text{-}Cs/TiO_2$ catalyst this mechanism is not possible because of the neutralization of -OH surface species due to the presence of Cs. Furthermore, a new intermediate for this reaction could be seen in the IR spectra of $Pt\text{-}Cs/TiO_2$ (-CHO species). For the better comprehension of the mechanics and the intermediates formed, transient studies were also carried out. The results (**Figure 1**) confirmed the previous hypothesis. Overall, our study demonstrates that Cs is an excellent promoter for the RWGS enabling high selectivity in the low-temperature range, opening new mechanistic pathways for gas-phase CO_2 upgrading.

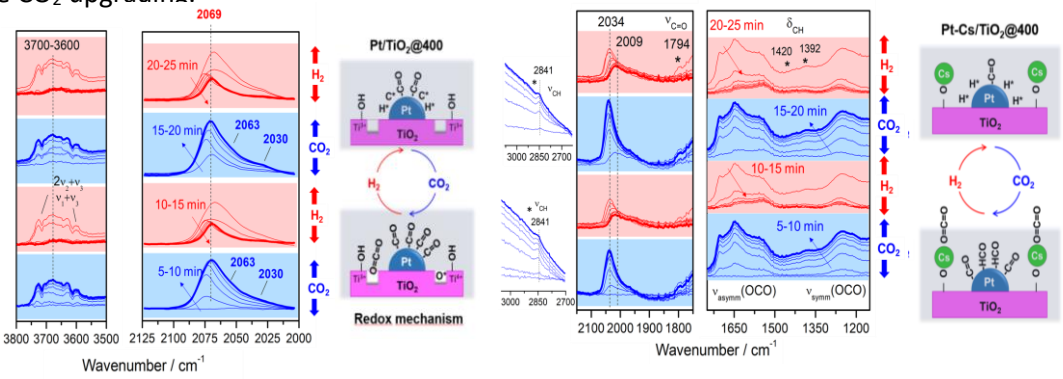

Figure 1. Transient experiment for Pt/TiO_2 (left) and $PtCs/TiO_2$ (right) with alternated pulses of H_2/Ar and CO_2/Ar at 250 ^oC

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Pore size effects in porous Ag electrodes for electrochemical CO_2 reduction

Maaike E.T. van Ittersum[1]*, Claudia J. Keijzer[1], Karen van den Akker[1], Peter Ngene[1] and Petra E. de Jongh[1]

[1]*Materials Chemistry & Catalysis, Debye Institue of Nanomaterials Utrecht, The Netherlands*

**m.e.t.vanittersum@uu.nl*

Introduction

Electrochemical CO_2 reduction is promising to close the carbon cycle. Good catalysts converting CO_2 at high current densities (**>**10 mA/cm^2**)** are required for industrial application [1]. Porous metal electrodes are promising to achieve this, because of their high surface area and good electronic conductivity [2]. Unfortunately, they are also more prone to diffusion limitations. Also, the often complex pore structures make it hard to disentangle the effect of different parameters. Hence, porous model catalysts -made by use of ordered templates- are useful to fundamentally understand the processes taking place. Previous research showed the influence of the mesostructure of template-based porous Ag made on gold coated glass-slides on the selectivity [3]. To our knowledge, no one has tried to make these catalysts on commonly used substrates (such as carbon paper for GDEs) or discussed the presence and effect of diffusion limitations. Therefore, we discuss that template-based porous Ag can be prepared with PMMA sphere templates on different substrates and we discuss the effect of pore size.

Experimental

PMMA template spheres were prepared as previously described in literature [4], slightly changing the reaction conditions to obtain different sphere sizes. Porous Ag electrodes were prepared by firstly drying a dispersion of PMMA spheres on top of a substrate (carbon paper, Ag foil). After drying, 2.2 mg/cm^2 of Ag was deposited at -0.2 V vs Ag/AgCl using a solution described in literature[5][6]. Subsequently, the PMMA template was dissolved in acetone. Electrochemical measurements were performed in a H-type cell using a Pt counter electrode, a Ag/AgCl reference electrode and a Nafion membrane. In both the cathodic and anodic compartment (18 mL), 15 mL 0.1 M $KHCO_3$ was used as electrolyte and a flow of 10 mL CO_2/min was applied in the cathodic compartment. During catalysis, the gas products were analyzed with a GC.

Results and Discussion

After the syntheses of PMMA spheres, their average particle diameters were determined based on SEM images (e.g. Figure 1A) and were found to be 87, 115, 123, 203, 308 and 372 nm. Using these PMMA sphere templates, inverse porous structures (e.g. Figure 1B) were obtained successfully on different substrates (carbon paper, Ag foil). To investigate diffusion limitations in catalysis, the partial current densities for the porous Ag samples with different pore diameters were compared. Figure 1C shows that at more negative potentials, the pore diameter becomes more important for the partial current density. At a potential of -1.4V vs RHE, an optimum in CO current density was found around 200 nm pore diameter. At this pore size, the current density is more than 1.5 times higher. This is an indication that, especially at more cathodic potentials, diffusion in and out the pores becomes an important factor to take into account.

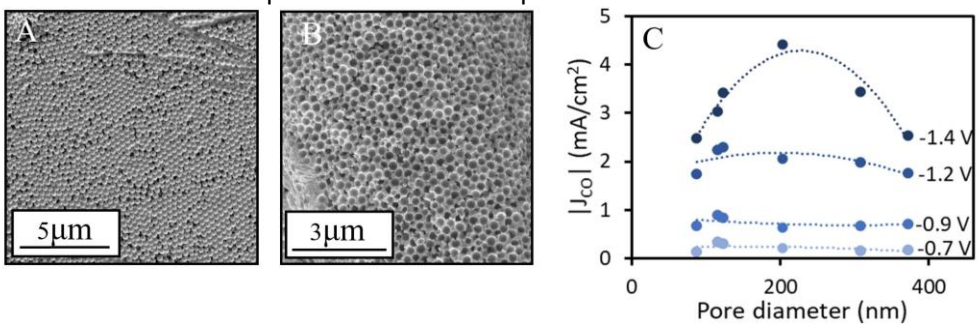

Figure 1. A) PMMA spheres with an average particle diameter of 308 nm; B) Porous Ag made by deposition of Ag in the holes of a 308 nm PMMA spheres template on C paper and subsequent removal of the PMMA spheres; C) Partial CO current density at -0.7, -0.9, -1.2 and -1.4 V vs RHE for porous Ag with different pore diameters.

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Multifunctional Materials for CO_2 Capture and Conversion

L. C. Buelens[a], V. Singh[a], S. Kumar Das[a,b], A. Longo[b], D. Poelman[c], H. Poelman[a], K. M. Van Geem[a], V. V. Galvita[a]*

[a]*Laboratory for Chemical Technology (LCT), Ghent University, Belgium;* [b]*European Synchrotron Radiation Facility, Grenoble, France;* [c]*LumiLab, Dept. Solid State Sciences, Ghent University, Belgium*
[*]*Vladimir.Galvita@UGent.be*

Keywords: sorption-enhanced, chemical looping, super-dry reforming

Introduction. Over the past decades, the interest in sorption-enhanced catalytic and chemical looping processes has tremendously increased, owing to their advantages with respect to (1) thermodynamic equilbrium limitations through Le Chatelier's principle and (2) inherent CO_2 capture and utilization at limited additional cost[1,2]. To upscale these processes, it is crucial to develop multifunctional materials, carrying a combination of CO_2 sorption, catalytic and/or redox properties. This work provides new insights into the design of low-cost "multifunctional materials" aided by rational active component distribution.

Experimental/methodology. In this work, multifunctional materials based on Fe and Ca were synthesized through 3 different methods. First, a benchmark of CaO/Al_2O_3 (CO_2 sorbent) and $Fe_2O_3/MgAl_2O_4$ (oxygen storage material) was prepared by physical mixing[3]. Secondly, a set materials was synthesized by sol-gel autocombustion (SGAC) using citric acid and calcium, magnesium, aluminum and iron nitrates as precursors (CFMA-SGAC). Finally, a wet physical mixing (WPM) method was applied using CaO/Al_2O_3 with $Fe(NO_3)_3.9H_2O$ (FCA-WPM) and $Fe_2O_3/MgAl_2O_4$ with $Ca(NO_3)_2.6H_2O$ precursor, respectively (CFMA-WPM). All materials were characterized through X-ray diffraction (XRD), synchrotron-based in situ X-ray Absorption and Raman Spectroscopy (XAS, XRS) and temperature-programmed reactions (TPRe) such as carbonation-decarbonation, reduction by H_2 and oxidation by CO_2.

Results and discussion. Detailed characterization by means of XRD and TPRe indicates that the CFMA-SGAC materials exhibit a clear loss of sorption functionality compared with the benchmark physical mixture (Figure 1), owing to mixed oxides containing Ca. Since this Ca is less readily available for $CaCO_3$ formation, the formation of such phases jeopardizes the CO_2 sorption capacity. Even when comparing samples with an increased nominal Ca content, hardly any CO_2 sorption functionality is observed, indicating that oxides of Fe, Mg and/or Al immobilize Ca through mixed phases in CFMA-SGAC materials. Nevertheless, some of these materials showed excellent oxygen storage and CO_2 conversion capacity, albeit at temperatures above 1123 K. For the materials synthesized through wet physical mixing, CFMA-WPM proves far superior to FCA-WPM in terms of CO_2 sorption capacity (Figure 1). Although the latter has a very high redox capacity, more than twice that of the benchmark material, it is solely available at temperatures exceeding 1173 K. Similar as for CFMA-SGAC materials this is attributed to the effect of Ca-containing mixed oxides, again leading to strongly diminished CO_2 sorption capacity. As for CFMA-WPM, on top of its promising CO_2 sorption capacity, ample redox capacity is observed at intermediate and high temperature, outperforming the benchmark physical mixture with ca. 85% in CO_2 sorption and ca. 30 % in oxygen storage capacity. Based on this performance, the material makes a true candidate for Ni addition and use in the chemical looping super-dry reforming process[3].

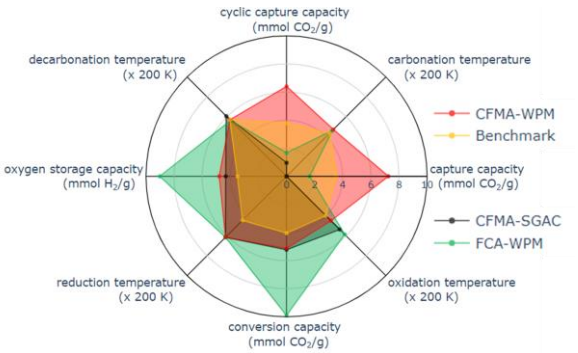

Figure 1. Result summary of CO_2 sorption behaviour, H_2 and CO_2 conversion capacity.

Acknowledgements
The authors acknowledge the assistence of the beamline staffs of BM08 and ID20 at ESRF (CH-6418 and CH-6500).

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Reverse Microemulsion Synthesis Promotes the Formation of Iron Carbide in Direct Hydrogenation of CO_2 to Light Hydrocarbons

Y. Yu, D.S.A. Simakov*

University of Waterloo, Waterloo, Ontario, Canada
**dsimakov@uwaterloo.ca*

Keywords: reverse microemulsion, CO_2 conversion, iron carbide, light hydrocarbons

Introduction. CO_2 utilization has recently attracted significant interest as an alternative approach to CO_2 storage [1]. Converting CO_2 into synthetic fuels is an attractive pathway to decrease CO_2 emissions and to reduce our dependence on fossil fuels. Thermocatalytic hydrogenation provides advantages of fast reaction rates and high conversion efficiencies, thus allowing for compact, high-throughput operation. The required H_2 can be generated via water electrolysis using renewable electricity (hydro, wind, solar), surplus electricity, or nuclear power.

In the study presented herein, reverse microemulsion (RME) method was implemented aiming for smaller nanoparticle size and narrower size distribution [2, 3]. In the RME system, small water droplets containing desired reactants are surrounded by surfactant molecules and dispersed in a continuous oil phase. RME method is favored by the advantages of the high specific surface area of the synthesized nanoparticles, since the nanodroplets act as microreactors, restraining the amounts of reactants and limiting the nanoparticle size.

Experimental/methodology. K-Fe/γ-Al_2O_3 catalyst was synthesized by the RME method [2, 3], alongside two reference samples fabricated by wet impregnation on the RME-synthesized γ-Al_2O_3 and commercial γ-Al_2O_3. The RME synthesis resulted in the highest specific surface area (239 m^2/g), consisting of well dispersed iron oxide nanoparticles (5-10 nm). The prepared catalysts were evaluated for their catalytic performance in CO_2 hydrogenation to lower olefins and paraffins (C2-C6). Fresh (calcined) and spent (post reaction) catalysts were characterized by a number of analytical techniques (XRD, TPR, TPD, STEM-EDS, TGA-FTIR, XPS).

Results and discussion. The RME-synthesized K-Fe/γ-Al_2O_3 catalyst showed excellent catalytic performance at a moderately elevated pressure (10 bar), with the C2-C6 selectivity of 52% and CO_2 conversion of ca. 55% at 375 °C and H_2/CO_2 = 4. Reference (wet impregnation) samples showed significantly lower CO_2 conversion and higher selectivity to CO and CH_4 formation. The RME method resulted in a superior catalytic performance, ascribed to the enhanced specific surface area, reinforced reducibility, and facile formation of the iron carbide (χ-Fe_5C_2) phase.

The maximum obtained CO_2 conversion and selectivity to C2+ hydrocarbons exceeded 50% over the RME-synthesized K-Fe/γ-Al_2O_3, attaining 7.4 mmol g^{-1} h^{-1} space time yield (STY) at 10 bar and 375°C. STEM-EDS analysis revealed the formation of both χ-Fe_5C_2 and Fe_3O_4 phases under reaction conditions.

Direct CO_2 hydrogenation to light hydrocarbons can provide an alternative route to conventional oil cracking, which is energy- and carbon-intensive. However, achieving high CO_2 conversion and high selectivity to C2+ hydrocarbons at the same time is very challenging. Elevated temperatures result in high CO_2 conversion but also lead to increasing formation of CO and CH_4. Our study provides important insights into the synthesis of Fe-based catalysts for CO_2 hydrogenation to light hydrocarbons.

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Structure sensitivity of methanol synthesis from CO_2 on Cu/ZrO_2 catalysts

Rodrigo Pallacán[1], Tomás Vergara[1], María F. Guevara[1], Romel Jiménez[1], Alejandro Karelovic[1]*
[1]*Carbon and Catalysis Laboratory (CarboCat), Department of Chemical Engineering, Concepción, Chile*
**akarelov@udec.cl*

Keywords: Methanol, CO_2 hydrogenation, *operando*-DRIFTS, ZrO_2

Introduction. Copper catalysts are the most studied for the methanol synthesis via CO_2 hydrogenation. An appropriate support for copper nanoparticles should be capable of enhancing the desired reaction and also avoid deactivation of the catalyst. Zirconium oxide has been shown to greatly increase the methanol formation rates compared to inert supports, like silica, probably via the formation of new interfacial Cu-ZrO_2 active sites. In this work, we assess the effect of Cu particle size on the kinetics of the process.

Experimental/methodology. Cu/ZrO_2 catalysts were prepared by wet impregnation varying the Cu content from 0.1 to 10 wt.%. Catalysts were characterized by TEM, XRD, H_2-TPR and N_2O-decomposition. Kinetic studies were performed in a fixed bed reactor in differential operation, without mass transfer limitations. Kinetic isotopic effect (KIE) experiments (H_2/D_2) as well as H_2 and CO_2 partial pressure variations were carried out in the same system. *Operando*-DRIFTS experiments were performed in a low dead volume cell connected to a mass spectrometer for on-line product measurement. Steady State Isotopic Transient Kinetic Analyses (SSITKA) coupled with *operando*-DRIFTS were also carried out.

Results and discussion. Kinetic experiments showed an asymptotic behavior of the methanol formation rate with increasing copper content (particle size)(Fig. 1-a). Apparent activation energies (E_{app}) are different for CO and CH_3OH formation. For methanol, the E_{app} increases significantly for catalysts with low particle size (Fig. 1-a). Fig. 1-a shows that, for methanol formation, the apparent reaction order with respect to hydrogen partial pressure does not depend on the particle size, which agrees with hydrogen activation occurring on Cu and that this phenomenon is not affected by the size of copper particles. On the other hand, the order with respect to CO_2 increases from ca. 0.2 to 0.43 when particle size decreases, showing that CO_2 activation and further reaction is occurring on sites affected by the decrease in particle size, probably on the interphase between Cu and ZrO_2. The change in the KIE with particle size also points out to a change in the nature of the active sites. The variation of methanol synthesis TOF with particle size for Cu/ZrO_2 shows a different behavior compared to Cu/SiO_2 [1], with increasing rates for lower particle sizes, which are correlated with higher interfacial length. *Operando*-DRIFTS experiments allowed the identification of bidentate formates and methoxy groups on the surface, in accordance to other studies [2]. Formate species at 2848 cm^{-1} were identified as active intermediates since the rate of their disappearance under transient conditions is similar to that of methanol formation. These species are nearly absent on the catalyst with lower particle size (0.1% Cu/ZrO_2, Fig. 1-b). This could be attributed to a change in the nature of the active site when Cu particle size is too low (< 2 nm) in which the interphase is no longer able to locate reactive intermediates.

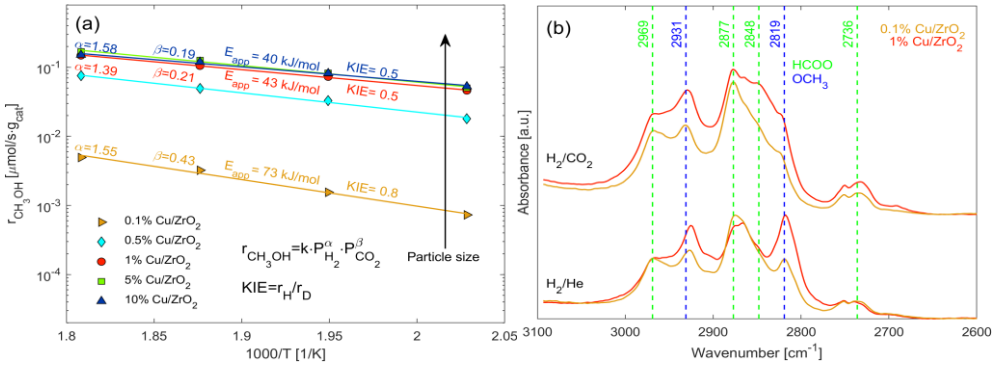

Fig. 1. (a) Arrhenius plot and kinetic parameters as a function of Cu content. (b) Operando-DRIFTS at steady state H_2/CO_2=3/1, 25 mL/min, 6 bar and 240°C.

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CO_2 hydrogenation to methanol on an ordered mesoporous $InCu/Al_2O_3$ catalysts: effect of indium promoter

Faisal Zafar[1], Mansoor Ali[1], Jong Wook Bae[1*]

[1]*School of Chemical Engineering, Sungkyunkwan University (SKKU), Suwon, Gyeonggi-do, Republic of Korea*
[*]*Corresponding Author's E-mail address (finejw@skku.edu)*

Keywords: CO_2 hydrogenation, Methanol, Indium, copper, catalyst, oxygenates.

Introduction. Carbon dioxide (CO_2) is by far the most emitted greenhouse gas, its utilization by CO_2 hydrogenation to methanol is considered a practical approach to mitigate its negative effects [1]. Copper (Cu) based methanol synthesis catalysts (e.g. Cu-ZnO-Al_2O_3) are less active for the selective methanol formation and are prone deactivatation due to the sintering and agglomeration of Cu and ZnO nanoparticles [2]. To enhance the thermal stability of Cu nanoparticles with reduced RWGS reaction and increased oxygenate formation rate, herein, we investigated the effects of In_2O_3 (In) promoter by varying In/Cu ratios on the mesoporous Cu/Al_2O_3.

Experimental/methodology. The highly ordered mesoporous γ-Al_2O_3 (mAl) support was synthesized by the well-known evaporation-induced self-assembly method (EISA) with slight modification from our previous work [3]. The CuO was impregnated first on the mAl support by incipient wetness impregnation method with subsequent calcination at 350 °C and further indium was successively impregnated with its different weight loadings (0 – 0.5 wt%). The CO_2 hydrogenation activity of the pre-reduced catalyst was performed at 250 °C and 5.0 MPa for 40 h in a fixed bed reactor using mixed gas with H_2/CO_2 molar ratio of 3. The effluent products were analyzed by an *in-situ* GC equipped with TCD and FID analyzer.

Results and discussion. The thermally stable spinal-type $CuAl_2O_4$ phase formations on the highly ordered mAl were confirmed by XAFS analysis (**Figure 1(A)**), and the $CuAl_2O_4$ phases were found to accelerate the CO formation rate by the RWGS reaction on the monometallic Cu/mAl catalyst (**Figure 1(B)**). Whereas, the loading of the optimum amount of In_2O_3 promoter (0.1 wt%) on the Cu/mAl suppresses the CO formation due to the newly formed Cu-In_2O_{3-x} interaction and larger oxygen vacant sites. CO_2 conversion was found to be higher on the InCu/mAl(1) with 7.4% compared to other InCu/mAl in the range of 3.9 – 7.4% as well as In_2O_3 itself (0.8% conversion with 55.0% selectivity to methanol) with their stable activity for 40 h (**Figure 1(B)**). Higher loading of In_2O_3 resulted in lower CO_2 conversion due to the decreased active sites and oxygen vacancies on the catalyst surfaces. Interestingly, product distributions were significantly altered according to In_2O_3 content on the InCu/mAl, and the main CO byproduct formed by RWGS reaction was steadily decreased with an increase of In/Cu ratio from 79.9% on the Cu/mAl to 29.7% on the InCu/mAl(5). That suppressed CO formation rate corresponds to the steady increases of CH_3OH selectivity from 18.8 to 62.5%, which was inversely related to the amount of metal oxides including less active $CuAl_2O_4$ phase. It is worth to note that the significant product shifts from CO to CH_3OH on the In_2O_3-promoted InCu/mAl were attributed to the suppressed RWGS activity as well as increased surface formate intermediates (**Figure 1(C)**).

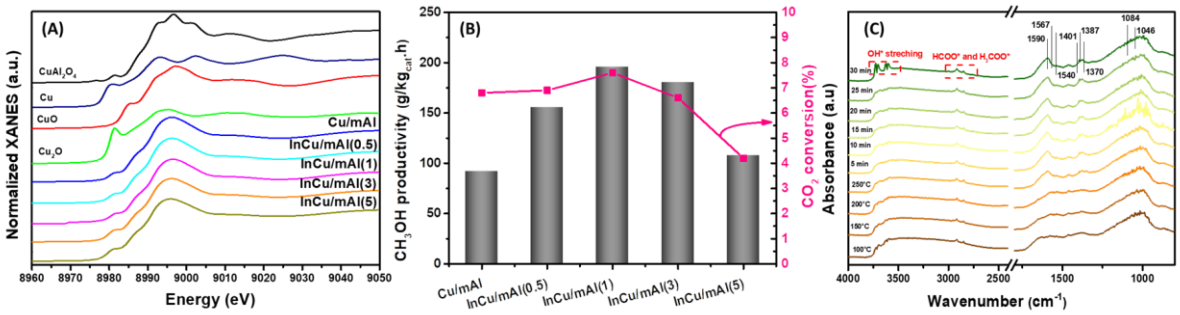

Figure 1. (A) Cu K-edge XAFS spectra, (B) CO_2 hydrogenation activity, (C) In-situ DRIFTS experiment on InCu/mAl(1)

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Utilization of CO_2 and H_2 for Arene Methyl-, Ethyl-, and Propylation

Jiachang Zuo, Youzhu Yuan*

State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, P. R. China
**E-mail: yzyuan@xmu.edu.cn*

Keywords: CO_2 hydrogenation, arene alkylation, modified zeolite, multifunctional catalyst

Introduction. Considering the trend of carbon neutrality, the involvement of CO_2 in preparing value-added bulk chemicals, such as para-xylene and other alkyl arenes, is feasible in terms of both economic and environmental benefits. Developing the catalyst for arene methyl-, ethyl-, and propylation reactions using CO_2 as a building block in a one-pot method will provide new routes for the regulation of arene components. Due to the difference in arene ring C(sp^2) and side chain C(sp^3), methylation in arene ring is prefered compared with alkylation (chain growth) in side chains of arene.[1] We reported a bifunctional catalyst for toluene methylation to para-xylene using CO_2 and H_2. The closer active sites between CO_2 hydrogenation and alkylation, the better catalytic performance.[2] However, in benzene ethyl- and propylation reactions by the same strategy, the two active sites must be separated because the high energy barrier CO_2 coupling reaction needs to be conducted preferentially. Here, we further report the in-depth results of this topic.

Experimental/methodology. Catalytic performance was evaluated on a high-pressure fixed-bed reactor. For the methylation reacion, $ZnZrO_x$ (ZZO) and Si-modified H-ZSM-5 (Z5) were mixed as bifunctional catalyst and used to conduct CO_2 hydrogenation and arene methylation, respectively. For the ethyl- and propylation, an additional SAPO-34 (S34) was used for CO_2 coupling to ethyl- and propylene. P-modified Z5 was used to regulate the ethyl- and propylbenzene products. In this case, ZZO and P-modified Z5 were separated by a dual-bed system or ZZO@S34 core–shell catalyst.

Results and discussion. ZZO solid-solution catalyst with excellent methanol selectivity at above 320 °C was used to perform CO_2 hydrogenation reaction, to match the high reaction temperature above 350 °C of arene alkylation. Compared with the industrial methylating reagent methanol, CO_2 can generate CH_3O* intermediate for the methylation at 360 °C via the hydrogenation route, while the methanol dehydrogenation route requires 420–480 °C. Thus, methanol to olefin side-reaction can be avoided and the usage of carbon source is improved. For the benzene ethyl- and propylation reaction using CO_2, S34 was used for the CO_2 to ethyl- and propylene reactions. The Gibbs free energy barrier for CH_3O* to undergo C(sp^3)–C(sp^3) coupling to form ethylene is 146 kJ mol^{-1}, which is higher than that of 96 kJ mol^{-1} for C(sp^2)–C(sp^3) benzene ring alkylation with CH_3O*. Therefore, the active site of CO_2 hydrogenation (ZZO) needs to be separated from that of alkylation (Z5), otherwise the product is polymethylbenzene. The selectivity of ethylbenzene in aromatics can reach up to 84% by using a dual-bed system. In addition, regulating the acidity of Z5 by P can modulate the product distribution toward propylbenzene up to 65%.

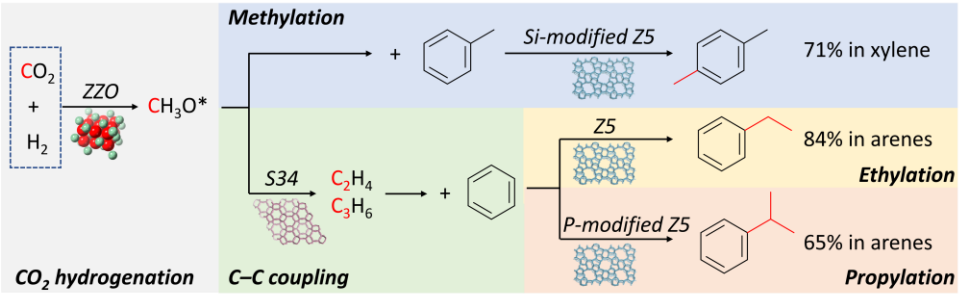

Figure 1. Reaction routes of arene methyl-, ethyl-, and propylation using CO_2 and H_2.

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Catalytic Conversion of Amine Carbamates into Organic Urea Derivatives by CeO_2 Catalyst in Corresponding Amine Solvents

M. Yabushita[1], J. Peng[1], Y. Li[1], R. Fujii[1,2], M. Tamura[3], Y. Nakagawa[1], K. Tomishige[1,4*]

[1]*School of Engineering, Tohoku University, Sendai, Japan*
[2]*Organic Research Laboratory, Tosoh Corporation, Shunan, Japan*
[3]*School of Engineering, Osaka Metropolitan University, Osaka, Japan*
[4]*Advanced Institute for Materials Research, Tohoku University, Sendai, Japan*
[*]*tomishige@tohoku.ac.jp*

Keywords: CO_2 capture and utilization (CCU), non-reductive conversion, CeO_2, acid-base bifunctionality

Introduction. Non-reductive conversion of CO_2 with amines to orgnic urea derivatives is an attractive approach as a CCU technology and also alternative to the current harmful production process of urea derivatives relying on phosgene. We recently found that ethylenediamine carbamate (EDA-CA), whose production is easy via the chemical absorption of CO_2 in ethylenediamine (EDA), was transformed into 2-imidazolidinone (so-called ethyleneurea, EU) over CeO_2 catalyst without pressurized CO_2 (Fig. 1), where 2-propanol was the reaction solvent [1]. 2-Propanol suppressed the undesired thermal decomposition of EDA-CA to EDA and CO_2 to some extent, but not completely. Another drawback of this system is the insolubility of EDA-CA in 2-propanol at room temperature, making the handling of this system quite difficult. This paper introduces our recent achivements of the development of new efficient catalytic system for EDA-CA conversion into EU by using EDA as a solvent [2], which can dissolve EDA-CA even at room temperature.

Experimental. The white powder of pure EDA-CA was prepared by pressurizing CO_2 at 5 MPa in a 190 mL high-pressure reactor containing EDA. For typical reactions, 20 mmol of EDA-CA, 2.0 mmol of CeO_2 (Daiichi Kigenso Kagaku Kogyo, calcined at 873 K for 3 h), and 100 mmol of EDA were charged into the reactor. After being filled with Ar 1 MPa, the reactor was heated to a designated temperature. The time when the inner temperature of the reactor reached the target one was defined as 0 h of reaction time. The products and unreacted substrate were quantified by GC-FID and ^{1}H NMR.

Results and discussion. Our catalyst screening test demonstrated only CeO_2 to exhibit the high catalyic performance for this reaction. Fig. 2 shows the time course of EDA-CA transformation in EDA solvent at 413 K. EU was the sole reaction product at 0 h, while another urea derivative *N*,*N*'-bis(2-aminoethyl)urea (LU) was also produced due to the subsequent reaction of EU with EDA in the liquid phase. The turnover frequency for the EDA-CA conversion was elucidated from the initial slope of this time course to be 3.7 h^{-1}. This value was at least 6-fold higher than those in reported works regardless of the lower reaction temperature (0.60 h-1 by CeO_2 catalyst in 2-propanol at 413 K [1]; 0.47 h^{-1} by $Cp_2Ti(OTf)_2$ in *N*,*N*'-dimethyl-2-imidazolidinone at 433 K [3]). Also, the monitoring test for inner pressure of the reactor indicated that the thermal degradation of EDA-CA was suppressed apparently completely. These data clearly demonstrated the great advantages of EDA as a reaction solvent compared to previously used ones. This catalytic system using CeO_2 catalyst and corresponding amine solvent was also found to be reusable and also applicable to the conversion of other amine carbamates into organic urea derivatives.

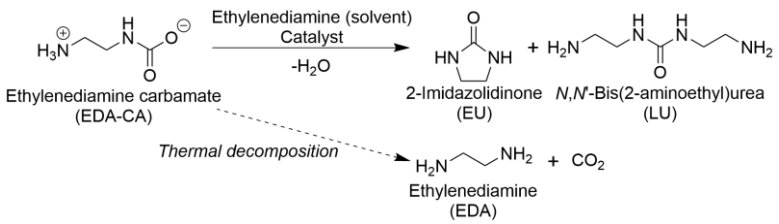

Fig. 1 Conversion of ethylenediamine carbamate (EDA-CA).

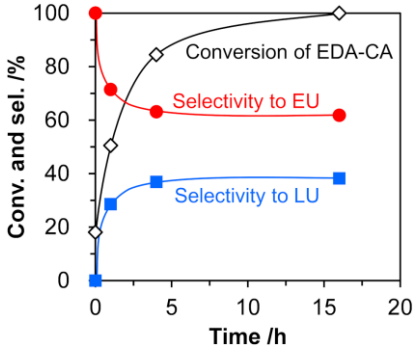

Fig. 2 Time course of EDA-CA conversion. Conditions: EDA-CA 20 mmol; CeO_2 2.0 mmol; EDA 100 mmol; Ar 1 MPa (r.t.); 413 K.

Acknowledgments

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Leaching in Specific Facets of ZIF-67 and ZIF-L Zeolitic Imidazolate Frameworks During the CO_2 Cycloaddition with Epichlorohydrin

Jose J. Delgado-Marín[1], Alejandra Rendón-Patiño[2], Vijay Kumar Velisoju[2], Gadde Sathish Kumar[2], Naydu Zambrano[2], Magnus Rueping[2], Jorge Gascón[2], Pedro Castaño[2], Javier Narciso[1] and Enrique V. Ramos-Fernández[1,*]

[1]Instituto Universitario de Materiales de Alicante, Universidad de Alicante, San Vicente del Raspeig, Spain
[2]*KAUST Catalysis Center, King Abdullah University of Science and Technlogy (KAUST), Thuwal, Saudi Arabia*
[*]*enrique.ramos@ua.es'*

Keywords: Crystals, Carbon dioxide, Epichlorohydrin, ZIFs, Catalysts

Introduction

Catalytic coupling of CO_2 with epoxides to form cyclic carbonates is one of the most efficient methods for CO_2 fixation. This reaction is catalysed by Lewis acid sites with the help of nucleophilic (co-catalyst). ZIF-8 and ZIF-67 are MOF very active as catalysts in this reaction although they do not have coordinative unsaturated sites or catalytically active functional groups. In addition, the pore opening of the structure is around 0.3 nm, which makes it difficult the diffusion. The scientific community generally ascribes the origin of this catalytic activity to defects in the ZIF crystals on the outer surface. So in this study, we decided to prepare crystals that ended up with different facets, to see which one was more active and thus be able to design better catalysts. What we found was that the crystals were easily degraded by the {100} facet and the leached species are the true origin of the catalytic activity.

Experimental/methodology

Four types of ZIF-67 have been synthesized: nanocubes (ZIF-67-NC), truncated rhombic dodecahedrons (ZIF-67-TRD), rhombic dodecahedrons (ZIF-67-RD) and ZIF-L. The catalysts have been tested in the cycloaddition of CO_2 with epichlorohydrin, at 15 bar of CO_2 and 120^{0}C. The stability of the catalyst in the reaction was studied by hot filtering test, analyzing results of ICP-MS, FTIR and microscopy before and after reaction.

Results and discussion

Figure 1 shows the conversion of epichlorohydrin in the cycloaddition of CO_2, with ZIF-L and ZIF-67-NC being the most active catalysts. The diffraction patterns of the used samples do not change with respect to the freshly prepared ones. This may be a false proof of stability. If we look at the SEM images (Figure 2), we see that the ZIF-67-NC sample, which ends in the {100} facet, degrades considerably. When we analyse the reaction mixture (ICP-MS) we also see that there is a considerable amount of Co in the reaction mixture. The same is true for the other samples. In all cases the samples were degraded by the {100} facet.

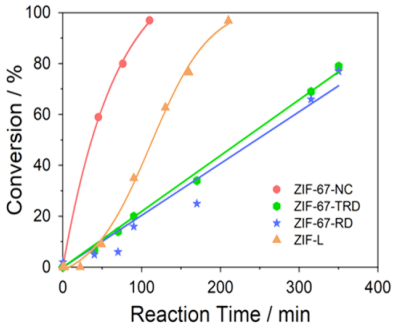

Figure 1. Cycloaddition of CO_2.

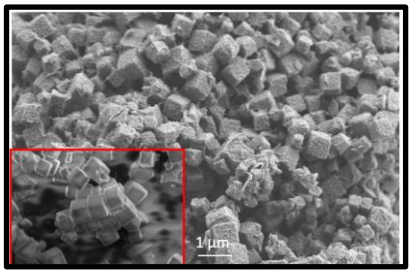

Figure 2. SEM image of ZIF-67-NC.

Thus, it can be concluded that leaching of some constituents of the MOF results in the formation of species in solution that are much more active than the MOF itself. In addition, the exposed facets on the MOF crystal play a large role, with the {100} facet degrading much faster (Figure 3).

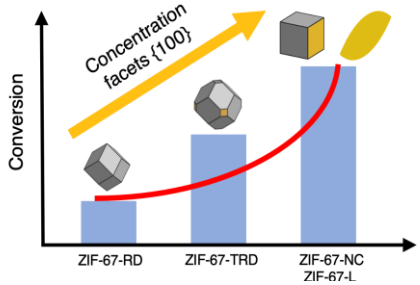

Figure 3. Schematic diagram.

Biogas methanation in an industrial-scale plate-type methanation reactor: interplay of reactor and catalyst optimization

E. Moioli[1*]

[1]*Hitachi Zosen Inova AG, Zürich, Switzerland*

Keywords: Biogas methanation, Reactor design, Heat transfer

Introduction

CO_2 methanation is an effective way to convert this greenhouse gas into a valuable product. The reaction is spontaneous, highly exothermic (ΔH^R_0 = -165 kJ/mol) and controlled by the thermodynamic equilibrium at high temperature. Hence, the scale up of the reaction is challenging, because a large heat exchange is required to achieve high conversion without running into heat transfer limitation problems [1]. We selected the plate-type fixed bed reactor operated with a Ni/ZrO_2 catalyst to obtain a large heat transfer, with the simplicity of a standard fixed bed reactor operating with a transition state catalyst. Ni/ZrO_2 is selected as catalyst because lab tests previously performed showed that this material shows an exceptional performance, offering catalytic activity already at 230 °C and preventing coking in the standard conditions for CO_2 methanation.

Experimental/methodology

The reactor is composed of thin plates, separated by 1,5 cm large chambers where the catalyst is filled. In the plates, boiling water is circulated, so that large heat transfer can be achieved and the temperature of the cooling medium can be controlled with precision. After the unavoidable (but limited) hotspot, the temperature is controlled by keeping the boiling water at the target temperature of maximum reaction yield (approximately 230 °C). The steam produced is collected in a steam drum on top of the reactor. Water is circulated from the steam drum in a descending pipe that feeds back the water to the bottom of the reactor. The maximum steam content in the cooling plates is kept below 5%, to maintain the circulation via natural draft. The catalyst employed is based on Ni/ZrO_2 [2]. It was observed that the optimal temperature for the CO_2 methanation over this catalyst is between 230-250 °C.

Results and discussion.

The reactor was operated for several hundred hours in the biogas methanation. Thanks to the large heat exchange and the precise temperature control, the reactor produced grid-compliant synthetic natural gas (SNG) over more than 1000 hours of operation. This was accomplished without exceeding the maximum temperature allowed by the catalyst (ca. 580 °C). A characteristic temperature profile is shown in figure 1b. The heat transfer limited region in the reactor is limited to the hotspot, as visible in the change of slope in the temperature profile after approximately after 0.8 m of reactor. The reactor was targeting a GHSV of 1000 h^{-1}, but the experiments showed the possibility to higher the space velocity to 2000 h^{-1}. Additionally, it was possible to operate the reactor in partial load without problems and still producing grid compliant SNG. In this presentation, we will show several characteristic results of the reactor operation, demonstrating how this reactor type is particularly suitable for the CO_2 methanation reaction.

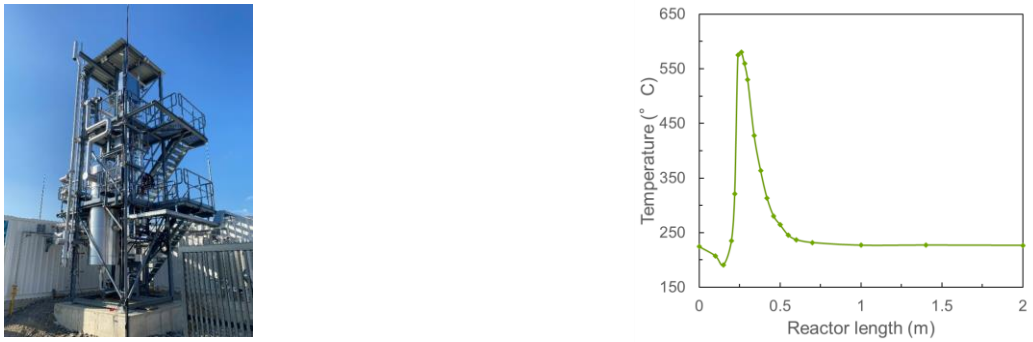

Figure 1. A) Image of the plate-type fixed bed reactor operating the CO_2 methanation B) The characteristic temperature profile of the plate-type methanation reactor.

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Lewis acid zeolites activate dihydrogen in N-formylation reaction

Jan Přech[1*], Martin Hulla[2]

[1]*Dept. of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Albertov 6, Prague 2, Czech Republic*
[2] *Dept. of Inorganic Chemistry, Faculty of Science, Charles University, Albertov 6, Prague 2, Czech Republic*
**corresponding author: jan.prech@natur.cuni.cz*

Keywords: Lewis acid, zeolite, N-formylation, CO_2 hydrogenation, frustrated Lewis pairs

Introduction.

Pairs of sterically hindered Lewis acids and bases, which cannot form classical acid-base adducts, are called frustrated Lewis pairs (FLPs). Their unquenched Lewis acidity and basicity are available to accept and donate electron density to H_2 molecules, which results in their heterolytic cleavage. Homogeneous FLPs are thus established hydrogenation catalysts [1]. On the contrary, examples of heterogeneous FLPs are scarce. Zeolites are crystalline microporous silicates with acidic properties. Lewis acidic sites are generated, i.a., by isomorphous substitution of tetravalent hetero-ions such as Sn^{4+}, Zr^{4+} or Ti^{4+}, which contain empty d-orbitals and can extend their coordination [2]. In the present study, we demonstrate that Sn- and Zr-substituted beta zeolites catalyse N-formylation of morpholine with CO_2 and molecular hydrogen and investigate whether the reaction occurs via a mechanism similar to that of FLP homogenous catalysts.

Experimental/methodology.

Sn-beta and Zr-beta zeolites were synthesized by seed assisted direct hydrothermal synthesis. Titanium silicalite-1 (TS-1, MFI structure) was kindly provided by Zeolyst Int. Concentration of the present Lewis sites was determined by infrared analysis using deuterated acetonitrile and CO adsorbed on the respective sites. N-formylation of morpholine was performed with CO_2 (6 bar) and H_2 (94 bar) at 190°C in sulfolane.

Results and discussion.

Table 1 lists representative results of the reactions performed over the Lewis acidic zeolites together with their basic characterization. Experiments without hydrogen or the catalyst gave no N-formyl morpholine (N-FM). The observed turn-over-frequencies (TOF) over all of the zeolite catalysts outperform tricyclohexyl tin (IV) triflate : collidine (1.2 h^{-1}), which is a state-of-the-art homogeneous FLP catalyst [3]. Morpholine is a base small enough to penetrate the zeolite beta micropores. Therefore, it is expected to coordinate to the acidic sites or stay in their close vicinity. Due to the confined space in the zeolite, such adduct can act as FLP activating molecular hydrogen, which subsequently hydrogenates CO_2 to formic acid. Formic acid then reacts with morpholine yielding N-FM, which is less basic than morpholine and thus can be replaced by another morpholine molecule on the acidic site. To our knowledge, this is the first time a sole Lewis acid zeolite has been observed to activate molecular hydrogen.

Table 1: Si/M molar ratio (determined by ICP-MS), concentration of the Lewis acid sites (determined by CD_3CN probe), and TOF of the morpholine formylation over the Lewis acid zeolites.

Catalyst	**Si/M (M=Sn, Zr, Ti)**	**C_{Lewis} (mmol.g^{-1})**	**TOF ($mmol_{N\text{-}FM}$. $mmol_{metal}^{-1}$ h^{-1})**
Sn-beta	72	0.255	1.66
Zr-beta	130	0.13 (derived from Si/Zr)	1.90
TS-1	28	0.55	0.19

Acknowledgments

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Promotional effect of Na-FeMgO$_x$ during CO_2 hydrogenation to C_{5+} hydrocarbons

Sheraz Ahmed[1], Muhammad Kashif Khan[2,3], Jaehoon Kim[1,2,3*]

[1]*SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon, South Korea*
[2]*School of Chemical Engineering, Sungkyunkwan University, Suwon, South Korea*
[3]*School of Mechanical Engineering, Sungkyunkwan University, Suwon, South Korea*
[*]*Jaehoonkim@skku.edu*

Keywords: CO_2 hydrogenation, Mg Promoter, Higher hydrocarbons, Deactivation behavior.

Introduction: CO_2 can be considered an alternative feedstock to fossil resources for producing fuels and chemicals [1], which can contribute not only to reduce the high concentration in the atmosphere, but also to provide a sustainable solution to depleting fossil fuel reserves. Several studies have successfully converted CO_2 into C_1 chemicals (e.g., methanol, methane, formic acid, and carbon monoxide) [2]. The inherently high thermodynamic stability and inertness of CO_2 make its hydrogenation very challenging towards C–C coupling reaction; as a result, the CO_2 hydrogenation products have high H/C ratios because of rapid methane formation [3]. To overcome these limitations, sodium-promoted iron-magnesium oxide (Na-FeMgO$_x$) catalyst was proposed with high C_{5+} selectivity and low methane selectivity. Furthermore, the deactivation behavior of Na-FeMgO$_x$ catalysts was studied with several characterization techniques.

Experimental/methodology: The Na-FeMgO$_x$ catalysts were prepared by the co-precipitation method. Iron and magnesium nitrate were mixed and then sodium carbonate was used as a precipitant. Precipitates were filtered, dried, and calcined to synthesize the calcined catalyst.

Results and discussion: The CO_2 hydrogenation reactions were conducted over Na-FeMgO$_x$ at 330 ℃, 3.5 MPa, H_2/CO_2 ratio of 1:1 at a gas hourly space velocity (GHSV) of 2000 mL g^{-1} h^{-1}, which exhibit high C_{5+} liquid hydrocarbon selectivity of 66.5% (excluding CO) at a CO_2 conversion of 19.6%, while the selectivity of CH_4 (6.7%) was suppressed. The Na-FeMgO$_x$ shows effective performance for a high C_{5+} yield of 25.1% with a conversion of 49.1% at 360 ℃, 3.5 MPa, H_2/CO_2 ratio of 3:1 at a gas hourly space velocity (GHSV) of 4000 mL g^{-1} h^{-1}. The deactivation behavior of Na–FeMgO$_x$ catalyst was studied which shows the re-oxidation of the χ-Fe_5C_2 phase to the highly pulverized Fe oxide phases, and subsequent "wetting" of the pulverized Fe oxides on the surface of $MgCO_3$ as shown in Fig. 1.

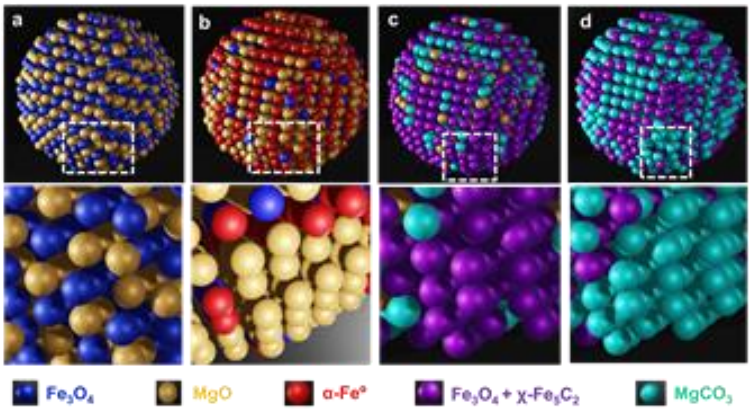

Fig. 1: Schematics of deactivation behavior of Na-FeMgO$_x$ (a) calcined Na-FeMgO$_x$, (b) reduced Na-FeMgO$_x$, (c) spent Na-FeMgO$_x$ (100h), and (d) spent Na-FeMgO$_x$ (670h).

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Fabrication of Cu-Zn coated structured foam catalysts for CO_2 hydrogenation to methanol in a fixed-bed reactor

Aakash Bhardwaj*, Rohit Sahu, Kamal Kishore Pant, Sreedevi Upadhyayula

Indian Institute of Technology Delhi, New Delhi, India
**Corresponding Author: bhardwajaakash137@gmail.com*

Keywords: Methanol, Ceramic Foams, Sintering, Hotspot formation.

Introduction. The conversion of anthropogenic CO_2 into value-added chemicals is key to begin the energy transition of chemical industries. This CO_2 hydrogenation to methanol reaction released a massive amount of heat due to its exothermicity ($CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$, $\triangle H_{298K}$ = -49.79 kJmol^{-1}). Hence, this released heat directly affects the catalyst properties due to the catalyst deactivation by sintering and hotspot formation [1]. Ceramic foams are superior to pellet ones owing to their attractive properties, such as high porosity, thermal resistivity, and high mechanical durability. These foam-based catalysts improve the hydrodynamics, heat and mass transfer properties, which helps enhance the catalytic performance [2]. In this work, we studied the effect of catalyst-loaded ceramic foams on the catalytic performance of methanol synthesis.

Experimental/methodology. The catalyst, slurry, and foam preparation were done in three steps: The Cu and Zn hydroxy carbonate precursors were mechano-chemically prepared in a ball mill, which subsequently dried and calcined to attain a catalyst denoted as CZ-BM-C. The as-prepared catalyst was then used for slurry preparation using polyvinyl alcohol (PVA), water, and glycerol in a fixed ratio [3], which was then dip-coated on corroded ceramic foams to attain the final structured foam catalyst. The catalyst characterization was done using XRD, FESEM, and HRTEM analysis. The catalytic activity tests were performed in a high-pressure fixed-bed tubular reactor connected with gas chromatography for product analysis.

Results and discussion. The FESEM images show the surface morphology of the ceramic foam, catalyst, and loaded foam (Figure 1 (a-e)). The effect of the foam combination on activity is given in Figure 1 (f). As depicted in the figure, we can see that the highest catalytic performance (conversion, selectivity, and space-time yield) was achieved in N (Zr-Zr) combination due to its low thermal conductivity. Further, the effect of temperature was studied (Figure 1 (g)) over the Nth combination at P = 40 bar and WHSV= 2600 ml/g_{cat}.hr, and it was observed that at T = 240 ^oC, P = 40 bar, and W =2600 ml/g_{cat}.hr highest catalytic performance was achieved and which follows the reaction thermodynamics.

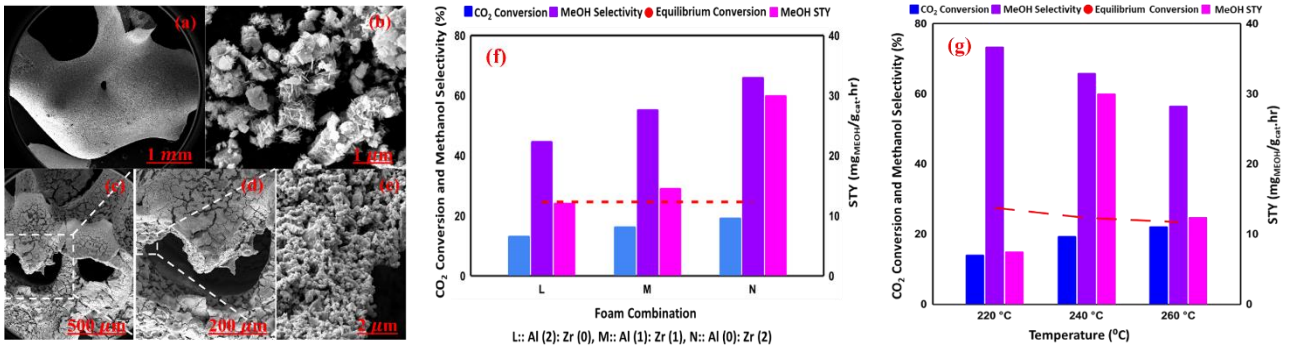

Figure 1. Fesem images of (a) Zr foam (b) Calcined catalyst (c, d, e) magnified view of the catalyst loaded Zr foam, (f) Effect of catalyst loaded foam combination on catalytic performance, (g) Effect of temperature on the catalytic performance at P= 40 bar and WHSV= 2600 ml/g_{cat}.hr.

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Demonstration of a continuous flow CO_2 hydrogenation to formate over a solid micellar catalyst

C. Mendes[1], F. Guo[1], S. Santos[1], Q. Wang[2], B. Sowa[1], V. Ordomsky[2], A. Khodakov[2], M.Saeys[1*]

[1] *Laboratory for Chemical Technology (LCT), Department of Materials, Textiles and Chemical Engineering, Ghent University, Ghent, Belgium*

[2] *Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, Lille, France*

**mark.saeys@ugent.be*

Keywords: Ruthenium, solid micelles, single-atom catalyst, CO_2 hydrogenation, formate.

Introduction

Hydrogenation of carbon dioxide (CO_2) to formate ($HCOO^-$) is a promising application of carbon capture and utilization for the production of formic acid (FA), an important feedstock chemical with increasing potential as an energy carrier. CO_2 hydrogenation to FA is normally carried out in liquid phase since the reaction is thermodynamically unfavorable in the gas phase. Often, FA is stabilized in the form of formate adducts by reaction with a base[1].

While homogeneous catalysts have industrially high activity and product selectivity at low temperature[2], their heterogeneous counterparts are preferred due to their well-established application in continuous flow and low dependence on solvents. Single-site catalysts have active sites with an uniform structure and a well-defined geometry characteristic of homogeneous catalysts, and the desired stability and easier handling of heterogeneous catalysts.

Solid Micellar (SOMIC) catalysts are an example of this new frontier[3, 4]. In this work, we report the potential of a solid micellar catalyst for CO_2 hydrogenation to formate both in batch and continuous flow.

Experimental/methodology

Our research approach includes catalyst synthesis, characterization (STEM-HAADF, EXAFS, XRD), and catalyst testing in combination with DFT modeling.

Results and discussion

The first SOMIC material, $Ru^{(III)}$@MCM-41 (**Figure 1a**), consists of $Ru^{(III)}$ sites incorporated in the walls of MCM-41 and stabilized by CTA^+ surfactant molecules in the pores. $Ru^{(III)}$@MCM was thoroughly tested in a 40 mL batch reactor and showed outstanding productivity of 0.9 g $HCOO^-g^{-1}h^{-1}$ in the presence of a tertiary ethyl amine (TEA) at 90 °C.

To make this catalyst industrially relevant and by using a multiphase continuous flow Robinson-Mahoney reactor, we recently demonstrated that $Ru^{(III)}$@MCM efficiently catalyzes CO_2 hydrogenation to formate in flow (**Figure 1b**), reaching a productivity of 0.3 g $HCOO^-g^{-1}h^{-1}$ at 70°C.

DFT modeling indicates that the unique activity and selectivity of this catalyst results from the heterolytic H_2 activation over Ru-OSi active sites.

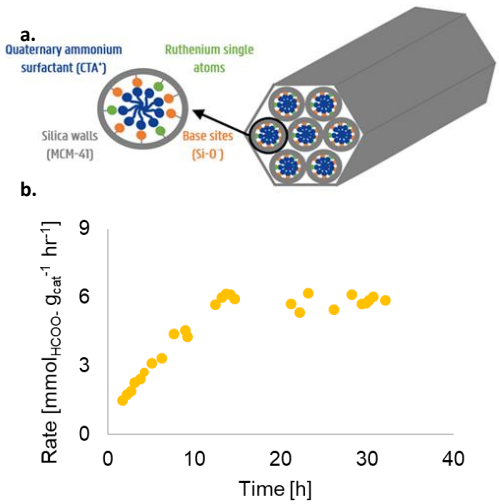

Figure 1. (a) Schematic representation of the $Ru^{(III)}$@MCM catalyst; **(b)** CO_2 hydrogenation to formate reaction rate over $Ru^{(III)}$@MCM in a continuous-flow experiment. Conditions: 2 g cat., 70°C, C_{TEA}= 1.3 M,F_{H2}/ F_{CO2}=0.4/0.4 mol/h.

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Low Temperature Activity of Tetragonal Type ZrO_2 Supported Ru Catalyst for CO_2 Methanation

Katsutoshi Sato[1*], Hitomi Higuchi,a Katsutoshi Nagaoka[1]

[1] *Graduate School of Engineering, Nagoya University, Nagoya, Aichi 464-8603, Japan*
[*] *sato.katsutoshi@material.nagoya-u.ac.jp*

Keywords: CCUS, Sustainable energy, Hydrogenation

Introduction. Many efforts have been made for long years to reduce CO_2 emissions which is one of the origins of global warming. Recently, CO_2 utilization have attracted attention as a hopeful way to contribute to the negative CO_2 emission. Conversion of CO_2 with H_2 to CH_4 is a potential route in the utilization of CO_2 [1]. CO_2 methanation is a significant exothermic reaction, and the equilibrium yield of CH_4 decreases with increasing reaction temperature. Therefore, to obtain a high yield of CH_4, the reaction should be carried out at a low temperature and the catalyst that shows high activity at such temperature is strongly demanded. Supported Ru catalyst is one of the candidate for CO_2 methanation due to superior CH_4 selectivity and high activity for a wide temperature range. We have previously reported that ZrO_2 calcined at low temperature with tetragonal type structure is potential support for Ru catalysts [2]. In this contribution, we have investigated the physicochemical properties of the highly avtive Ru/ZrO_2 catalysts and the reaction mechanism over the catalysts.

Experimental/methodology. The precursor of the ZrO_2 support was prepared by wet precipitation method using $ZrO(NO_3)$. Obtained precursor was calcined at 300, 500, and 800 ºC in static air. Hereafter, these are denoted $ZrO_2(300)$, $ZrO_2(500)$, and $ZrO_2(800)$. 5wt% Ru was supported on the ZrO_2 by the wet impregnation and followed by heating under Ar stream. The loading of Ru is set to 5 wt% of the weight of the catalyst. CO_2 methanation activity of the Ru/ZrO_2 catalysts were measured with a conventional flow system under atmospheric pressure.

Results and discussion. The calcination temperature of the ZrO_2 support influenced the catalytic activity of the Ru/ZrO_2 catalysts (Fig. 1). $Ru/ZrO_2(300)$ was the most active among tested catalysts. X-ray diffraction patterns elucidated that a significant part of $ZrO_2(300)$ is a tetragonal-type structure. With an increase in calcination temperature, the crystallite structure of ZrO_2 changed to monoclinic-type from tetragonal-type. This indicates that tetragonal-type ZrO_2 is the origin of the high CO_2 methanation activity of $RuZrO_2(300)$. To elucidate the influence of the crystallite structure of ZrO_2 for CO_2 activation step, the state of adsorbed CO_2 species was investigated by DRIFT analysis. A large amount of formate and bicarbonate species were absorbed on the surface of $ZrO_2(300)$. In contrast, the amount of adsorbed CO_2 species over the other two catalysts were small. It was reported that formate species are more easily hydrogenated to methane than other adsorbed species [3]. We surmise that tetragonal type ZrO_2 is suitable for the adsorption of CO_2 as formate species, and such character contributes to high CO_2 methanation activity at low temperatures.

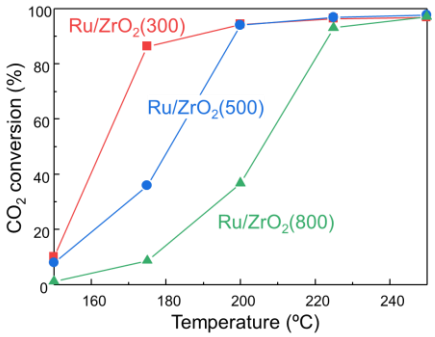

Fig. 1. Temperature dependence of CO_2 methanation activity over supported Ru/ZrO_2 catalysts.

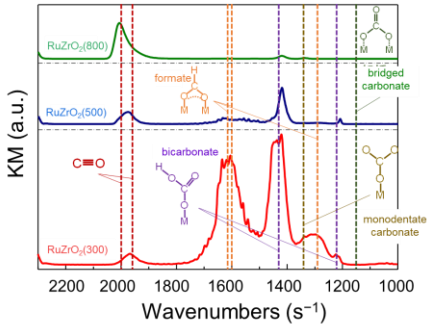

Fig. 2. DRIFT spectra for adsorbed CO_2 species over Ru/ZrO_2 catalysts..

Acknowledgments
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Effect of metal loading on perovskite-type oxide catalysts for reverse water gas shift reaction

S. Sekizawa[1], W. Doi[2] , T. Furukawa[1] , A. Yanagita[1] , K. Tashiro[1,2] , S. Satokawa[1,2*]

[1] *Graduate School of Science and Technology, Seikei University, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo 180-8633, Japan*

[2] *Faculty of Science and Technology, Seikei University, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo 180-8633, Japan*

[*] *satokawa@st.seikei.ac.jp*

Keywords: Reverse water gas shift (RWGS) reaction, perovskite-type oxide catalysts, metal loading effect

Introduction.

The conversion of CO_2 to fuels via catalytic reactions has attracted attention as a way of achieving carbon neutrality. In particular, the process for synthesizing liquid fuels by sequential catalytic reaction of reverse water-gas shift (RWGS) reaction followed by Fischer-Tropsch synthesis (FTS) using renewable H_2 and atmospheric CO_2 is expected as a promising technology. The former reaction produces CO from CO_2, and the latter affords hydrocarbons from CO. However, the challenge with this process is the divergence of the appropriate reaction temperatures (RWGS: >800 °C, FTS: 200-350 °C). Although the CO_2 conversion on RWGS reaction becomes lower as temperature decreases theoretically, the most important factor in this process is CO selectivity since the FTS can proceed even if the feed gas contains CO_2.[1] In this study, we considered the effective temperature for RWGS to be 500 °C, at which the RWGS reaction progresses up to 50%. Then, we investigated the effect of active metal addition on $BaZrO_3$-based perovskite-type oxide which was a high-temperature RWGS catalyst.[2]

Experimental/methodology.

The perovskite-type oxide containing Ba^{2+}, Zr^{4+}, and Y^{3+} ($BaZr_{0.9}Y_{0.1}O_{3-\delta}$; BZY10) was prepared by coprecipitation method from barium nitrate, zirconyl nitrate dihydrate, and yttrium nitrate hexahydrate, and then resulting solid was calcined at 1000 °C. The metal loading onto BZY10 was carried out by evaporation-drying method using metal nitrate aqueous solutions. The resulting catalysts were defined as M/BZY10 (M = Pt, Ru, Rh, Ir, Pd, Ni, or Co). The catalytic activity was evaluated using a fixed bed flow reactor at 0.1 MPa. 0.10 g of catalyst was packed into the center of the reactor tube and the temperature was increased to 700 °C under N_2 gas flow of 40 mL min^{-1}. After that, the catalyst was exposed to reactant gas ($H_2/CO_2/N_2$=3/1/1) at the flow rate of 40 mL min^{-1}. The outlet gas was analyzed using a gas chromatograph. The catalytic activities were evaluated by decreasing the reaction temperature from 700 °C to 300 °C.

Results and discussion.

Fig. 1 shows the CO_2 conversion and product selectivity on the RWGS reaction over BZY10 and 0.1wt%M/BZY10 at 500 °C. BZY10 showed 100% of CO selectivity, but the conversion was only 2%. When Pt, Ru, and Rh were added, significant increases in CO_2 conversion were observed, while only slight enhancements of the catalytic activity for RWGS reaction were revealed in the case of M = Ir, Pd, Ni, and Co. Although, the CO_2 conversions on Ru/BZY10 and Rh/BZY10 were higher than the that of Pt/BZY10, a large amounts of CH_4 was produced. In contrast, Pt/BZY10 showed high CO_2 conversion and 100% of CO selectivity. Therefore, Pt had the best active metal for the RWGS.

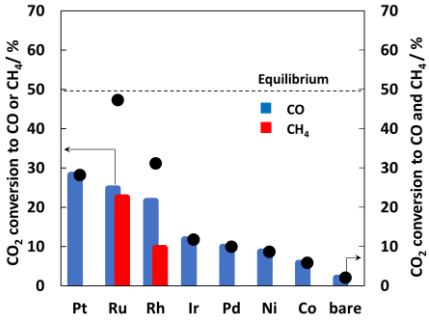

Fig. 1 CO_2 conversion and product selectivity on 0.1wt%M/BZY10 (M = Pt, Ru, Rh, Ir, Pd, Ni, and Co) at 500°C

Acknowledgments

This study has been conducted under a contract with the New Energy and Industrial Technology Development Organization (NEDO), Japan. We would like to express our gratitude to NEDO.

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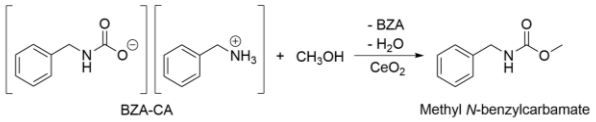
Synthesis of carbamates from CO_2-captured amines and alcohols over CeO_2 catalyst

S. Mihara[1], M. Yabushita[1], Y. Nakagawa[1], and K. Tomishige[1,2*]

[1]*Department of Applied Chemistry, School of Engineering, Tohoku University, Sendai, Japan*
[2]*Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai, Japan*
[*]*tomishige@tohoku.ac.jp*

Keywords: CO_2 capture and utilization, carbamate, CeO_2 catalyst

Introduction. Utilization of CO_2 as a cheap and non-toxic C1 resource has been desired to reduce its emission. In this view, synthesis of carbamates from CO_2 is a promising method because they are widely used for pharmaceuticals and dyes. Recently, catalytic conversion of CO_2-captured amines, which are easily synthesized from amines and CO_2 by chemical absorption, into urea derivatives was reported without high-pressure CO_2.[1-3] Yet, there is no report that has applied such substrates to catalytic production of carbamates. Here, we tackled carbamate synthesis from CO_2-captured benzylamine (BZA-CA) and methanol over CeO_2 (Scheme 1).



Scheme 1: Carbamate synthesis from BZA-CA.

Experimental. CO_2-captured benzylamine (BZA-CA) was synthesized from benzylamine (BZA) and CO_2.[2b] BZA-CA (10 mmol), CeO_2 (2 mmol), BZA (100 mmol), and methanol (1500 mmol) were put into an autoclave (190 mL) with a magnetic spinner. Reactants were heated at appropriate temperature, and then cooled to room temperature. Reaction solution was collected with methanol and analyzed by ^{1}H NMR and GC-FID by using *tert*-butyl alcohol as an internal standard.

Results and discussion. The time courses of the BZA-CA conversion were investigated at four different temperatures. The low reaction temperatures such as 393 K and 403 K gave low reaction rate and thus required long reaction times to obtain moderate yields of the desired product. On the contrary, the yield and selectivity of carbamate was decreased at 423 K due to undesired side reactions. Therefore, the moderate reaction temperature of 413 K was optimum. Fig. 1 shows the time course at 413 K. The amount of target product (red circles) was rapidly increased until 12 h and then gradually decreased. At longer reaction times, the produced carbamate successively reacted with benzylamine to form dibenzylurea and *N*-methylbenzylamine, the latter of which was formed via the thermal reaction of the produced carbamate. The highest yield of the target product was 64% in 12 h at 413 K. The larger amount of methanol provided the higher carbamate yield, and 1500 mmol of methanol was the optimum amount. The CeO_2 catalyst was confirmed to be reusable for this reaction at least four runs. This catalytic system was also demonstrated to be applicable to the transformation of various CO_2-captured amines with methanol to corresponding carbamates in good yield and selectivity.

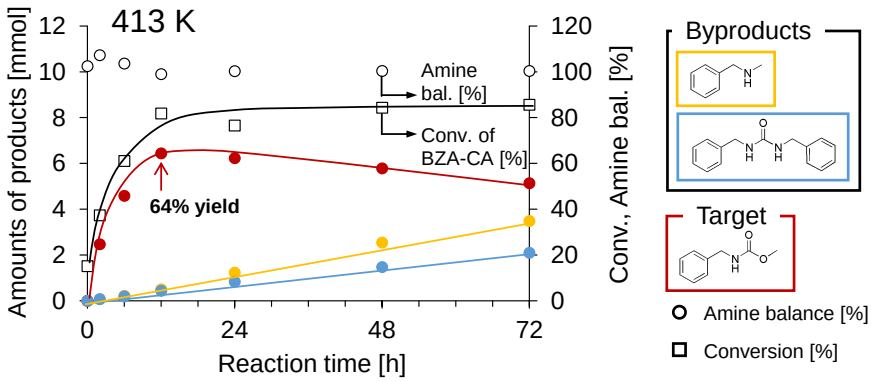


Fig. 1: Time course of carbamate synthesis from BZA-CA at 413 K. Conditions: BZA-CA 10 mmol, CeO_2 2 mmol, BZA 100 mmol, MeOH 1500 mmol, Ar 1 MPa (at r.t.), 413 K, 0-72 h.

Acknowledgments
This work was financially supported by NEDO (JPNP18016).

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Realistic conditions for Sabatier reaction: a promising alternative for cement industry decarbonization

D.Spataru[1,2*], A. Quindimil[1], C. Bacariza[2], J. Lopes[2], C. Henriques[2]

[1]c[5]Lab - Sustainable Construction Materials Association, Linda-a-Velha, Portugal
[2]CATHPRO/CQE-IST, Universidade de Lisboa, Lisboa, Portugal
daniela.spataru@tecnico.ulisboa.pt

Keywords: Decarbonization, Cement, CO_2 valorization.

Introduction. Nowadays, reducing greenhouse gases (GHG) emissions, namely CO_2, is mandatory in order to reach the ambitious goal of zero net emissions, i.e., climate-neutrality by 2050. One of the sectors that has a greater impact on CO_2 emissions is the cement industry, responsible for 8-11% of the CO_2 global emissions. CO_2 conversion into synthetic fuels, integrated with renewable energy pathways and efficient catalytic systems, became both a challenge and an opportunity to decarbonize several industrial (e.g., cement) and energy sectors. Indeed, CO_2 hydrogenation using green hydrogen, produced via water electrolysis with renewable energy (Power-to-Gas), is one of the most promising CO_2 utilization routes. More specifically, the CO_2 hydrogenation to CH_4, which is a clean energy vector with high calorific value, is considered an effective solution to store the excess of renewable electricity in the natural gas grid. Therefore, the CO_2 methanation reveals high potential for the future towards a circular economy and low carbon society [1].

CO_2 methanation, also known as Sabatier reaction, requires the use of catalysts due to the stability of carbon dioxide molecules. Thus, active metals such as Ni, Ru or Rh and supports such as Al_2O_3, SiO_2, zeolites, hydrotalcites, ZrO_2, CeO_2, SBA-15 etc. have been widely analysed in the literature. Among them, the utilization of zeolite-based catalysts has been gaining attention, mainly due to their easily tuneable properties [2].

One of the main components of flue gases from cement industries is oxygen (10-15 vol. %), which cannot be 100 % removed in the previous capture/pre-treatment step. Therefore its influence on CO_2 methanation reaction was evaluated.

Experimental/methodology. In the present work, three materials (Ni/Zeolite, Ru/Zeolite and a Commercial methanation catalyst) were used as catalysts for CO_2 methanation. Several characterization techniques (XRD, TGA, H_2-TPR, N_2 adsorption) were employed before and after reaction. Additionally, catalytic tests (2.5 bar and 250-450 ^oC) with and without O_2 (~4 vol. %) in the feed were performed.

Results and discussion. Results indicate that the nature of the active metal influences the resistance towards the presence of O_2. Ru exhibited a higher resistance towards oxidation, in accordance with literature, while the commercial sample presented the highest deactivation.

Acknowledgments
Authors thank FCT (UIDB/00100/2020 and UIDP/00100/2020) and c[5]Lab.

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Investigation on the effect of nickel and silica loading of Ni/SiO_2-Al_2O_3 catalysts for CO_2 hydrogenation

E. Spennati[1], P.Riani[2], V.S. Escribano[3], M.V. Garcia[3], G.Busca[1], G. Garbarino[1*]

[1] *Department of Civil, Chemical and Environmental Engineering, University of Genoa, Genoa, Italy*
[2] *Department of Chemistry and Industrial Chemistry, University of Genoa, Genoa, Italy*
[3] *Departamento de Quımica Inorganica, Universidad de Salamanca Plaza de La Merced, Salamanca, Spain*
[*] *gabriella.garbarino@unige.it, elena.spennati@edu.unige.it*

Keywords: CO_2 conversion, Nickel catalysts, Silica doping

Introduction. Nowadays, environmental pollution represents one of the main environmental problems. In this context, CO_2 emissions achieved the remarkable value of 36.3 Gt in 2021, increasing greenhouse gases concentration and correlated global warming [1]. A possible strategy to mitigate this environmental concern is the conversion of CO_2 into methane by the socalled Sabatier reaction using hydrogen arising from renewables. Conventional catalysts for this application are based on Ru- and Ni- [2-4]. Ni-based catalysts thanks to the Ni low cost and remarkable natural abundance, their high activity and robustness, represent a suitable choice for CO_2 hydrogenation reaction. Several supports have been investigated to enhance the catalytic performances. Among them Al_2O_3, SiO_2 [5], TiO_2, zeolites [6] are the most invesigated. However, Ni-based catalysts present several issues that need to be solved: *i*) low activity at low temperature, *ii*) low dispersion of the active phase and, *iii*) high deactivation manly due to particles sintering or coking. For these reasons and to make nickel-based catalysts suitable candidates at industrial scale, more efficient and competitive than noble metals-based catalysts more effort need to be done.

Experimental/methodology. In this work [7], we prepared a series of Ni/Al_2O_3 catalysts, with a Ni loading from 1 to 33 NiO wt.%, and we investigated the influence of the addition of SiO_2 (1 and 20 wt.%) both from the material and catalytic performances point of view. Catalysts were prepared by incipient wetness impregnation and both fresh end exhaust materials were characterized by means of BET, XRD, FE-SEM, EDXS, TPR, FT-IR, and UV-vis-NIR. Catalysts were tested in a tubular quartz reactor in diluted conditions and with a H_2/CO_2 ratio of 5. Reaction temperature has been varied in-between 523 to 773 K with 50 K temperature and backward to evaluate eventual short-term deactivation.

Results and discussion. Characterization results showed that SiO_2 support displayed a low Ni dispersion ability producing segregated NiO particles and a small amount of dispersed Ni^{2+}. While, increasing the Ni loading on the Si-doped alumina support a “surface spinel monolayer phase” is produced, and NiO is formed only when the support surface is completely covered by the spinel phase. Low loading Ni catalysts supported on SiO_2 showed moderate activity for rWGS (reverse Water Gas Shift) reaction and high CO selectivity, mainly due to nickel species dispersed in silica exchange sites. High Ni loading on the same support showed both rWGS and methanation activity but high short-term catalyst deactivation for methanation due to a coverage by a carbon veil on the large and segregated Ni metal particles. Ni dispersion, in the form of surface spinel phase, was higher on Ni-based alumina -rich carriers. These catalysts showed high metanation activity and selectivity to methane and short-term catalyst stability. The high methanation activity was attributed to small Ni clusters or metal particles interacting with alumina formed under reaction conditions. The 16 wt.% NiO supported on 1 wt.% of SiO_2/Al_2O_3 resulted to be the best catalyst by achieving a methane yield of 73% and a selectivity to methane around 100% at 673 K at atmospheric pressure and at a GHSV of 55000 h^{-1}.

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On the potential of dual-function FeCo catalysts for CO_2 utilization via inductive heating

S. Spyroglou[1*], C. Rameshan[2], M. Sanchez-Sanchez[1]

[1]*Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, Getreidemarkt 9/166, Vienna 1060, Austria*
[2]*Institute of Materials Chemistry, TU Wien, Getreidemarkt 9/166, Vienna 1060, Austria*
[*]*Corresponding Author: stylianos.spyroglou@tuwien.ac.at*

Keywords: CO_2 utlization, Fe catalyst, inductive heating, reverse water-gas shift

Introduction.
CO_2 utilization to produce CO via the reverse water gas shift (rWGS) reaction has gathered increasing attention in recent years. Fe-based catalysts are an attractive option because of their high thermal stability and high oxygen mobility,[1] in addition to their abundance and low cost. The ferromagnetic properties of Fe and Fe oxide nanoparticles in a relatively large temperature range enable their use as inductive heaters, via hysteresis losses when placed under an alternating magnetic field. The approach of using Fe nanoparticles both for catalysis and heating is expected to bring advantages such as the elimination of heat transfer limitations, fast response and the possibility of using electricity from renewable sources [2].
This work studies the magnetic and catalytic properties of Co-doped Fe nanoparticles as potential bifunctional materials for the catalysis of rWGS reaction using induction.

Experimental
Fe-Co materials were synthesized by wet impregnation of commercial SiO_2 and γ-Al_2O_3 supports with a total metal loading of 20% wt. and different Fe:Co ratios. The metallic loading is adjusted to ensure that the material can reach self-heating properties up to the temperatures necessary for rWGS.
Structure and redox properties of the catalysts were studied by in-situ XRD and H_2 temperature-programmed reduction. The magnetic heating capability was measured by the hysteresis loop area after applying a magnetic field in a vibrating sample magnetometer (VSM) at temperatures relevant for the catalytic reaction. Activity measurements were carried out in a tube reactor (3 mm internal diameter) in the temperature range of 250 – 350 °C. Prior to the reaction, the catalysts were activated in flowing H_2 at two different temperatures (350 and 500 °C).

Results and discussion.
Doping Fe catalysts with Co was found to increase the rWGS activity while maintaining high CO selectivity (>90%). In addition, the high Curie temperature of Co aids the inductive heating properties of the FeCo-catalysts, as it is confirmed by magnetic hysteresis cycles measured at 500 °C. The temperature of activation in H_2 of Fe catalysts has a significant impact on both the catalytic activity and the heating capability of the material. This is attributed to the different particle size and metal/metal oxide phases present in the material after reduction. It was found that SiO_2 supported Fe particles are more reducible than those supported in Al_2O_3. Among the tested materials, FeCo supported on SiO_2 and reduced at 500°C, shows the highest heating potential, based on the large area of the hysteresis loop [3]. However, development of large Fe or FeCo particles (20 nm) results in low activity in rWGS. Conversely, γ-Al_2O_3 supported materials yielded smaller Fe particles (ca. 12 nm) after reduction at 500 °C, due to stronger metal-support interactions. Overall, Fe and Fe-Co particles supported on Al_2O_3 exhibit a good compromise between catalytic performance and magnetic heating capability, showing promise for their use as multifunctional materials for the heating and catalysis of CO_2 utilization via rWGS.

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Cobalt carbide catalyst development for CO_2 methanation: synthesis and characterization

S. Suman[1], A. Banerjee[1], L. Lefferts[1*]

[1]*University of Twente, Enschede, Netherlands*
[*]*Corresponding Author's E-mail address: l.lefferts@utwente.nl*

Keywords: CO_2 reduction, Transition metal carbides, Cobalt carbide, Heterogeneous catalysis

Introduction. The major energy demand of the world population is fulfilled by non-renewable resources of energy. These non-renewable resources cause pollution, global warming and lead to depletion of our natural resources [1]. So, there is a big need to find a solution to the pollutants that are emitted on burning of non-renewable resources. One of the major pollutants is CO_2 (a greenhouse gas) and there is a growing interest in the utilization of CO_2, as an abundant C1 source, to synthesize value-added chemicals and fuel (CH_4) by means of catalysis. Transition-metal carbides (TMCs) have a lot of potential in the field of catalysis, due to their exceptional electronic conductivity, remarkable chemical stability, and abundance of surface-active sites [2].

Experimental/methodology. Traditional synthesis techniques like carburization [3], the polyol method [4], ball milling [4] etc., are reported for Co_2C synthesis. These kinds of methods often cause the carbon species, which are concentrated more on the particle surface than in the bulk, to form coke and polymerize at high temperatures, significantly obstructing the catalyst's active sites. Here, we present an efficient and reasonably straightforward method for synthesizing carbides using melamine as carbon source. Co_3O_4-Al_2O_3 was synthesized by incipient wet impregnation method and then reduced and carbonized in a tube furnace at 500 °C for 1 h in a N_2 atmosphere. By carbonizing Co-oxide/Al_2O_3 catalysts using melamine under various reaction conditions, a series of Co_2C/Al_2O_3 catalysts were synthesized.

Results and discussion. It is seen that due to a strong thermodynamic driving force Co-oxides transform into carbides, thermodynamically driven by formation of stable CO and H_2O as by-products. Characterization results obtained with scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman analysis, were used to examine the catalysts' physicochemical features. Changes in the carbonization temperature led to the creation of cobalt phases with varying composition. The influence on the catalytic performance in CO_2 reduction will be reported and the structure-performance relationship will be discussed

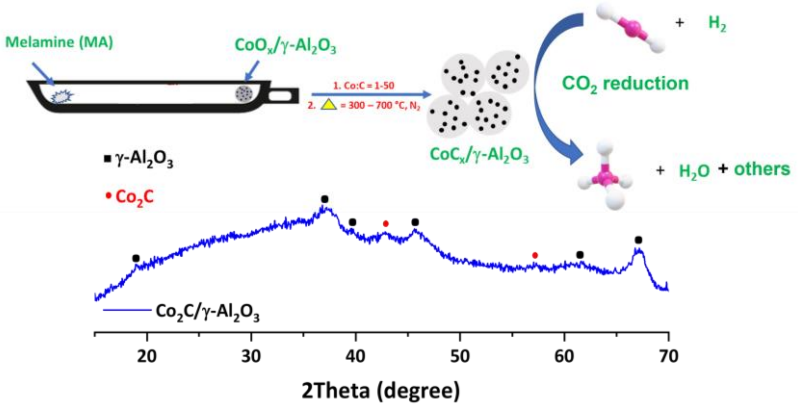

Figure 1. Graphical representation of Co_2C/γ-Al_2O_3 synthesis for CO_2 reduction to methane

Acknowledgments
We thank ing. B. Geerdink and K. J. Altena for their experimental and analytical support.

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Dry reforming of methane over Cr-Ni loaded on dealuminated Beta zeolite

Kazuya Tamura[1*], Shinya Kokuryo[1], Koji Miyake[1], Yoshiaki Uchida[1], and Norikazu Nishiyama[1]
[1]*Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan*
[*]*Corresponding Author: tamura.k@cheng.es.osaka-u.ac.jp*

Keywords: Dry reforming of methane (DRM), dealuminated Beta, coke deposition

Introduction. Global warming and climate change caused by greenhouse gas emissions from human activities have become serious issues. Effective utilization of CO_2, the largest emission of greenhouse gases, has been the focus of much attention in recent years. One promising method is dry reforming of methane (DRM), a catalytic process that converts CH_4 and CO_2 into valuable syngas (CO and H_2) with a CO/H_2 molar ratio of 1:1. The syngas can be converted into a variety of feedstock chemicals used in the petrochemical industry. However, since this reaction is endothermic, operating conditions at high temperatures (700-1000 ^oC) are required to achieve a high conversion efficiency of CH_4 and CO_2 [1]. Ni-based catalysts are considered the most promising for DRM reactions because they exhibit high DRM activity even at low reaction temperatures, are abundant in resources, and are relatively inexpensive. However, a major drawback of Ni-based catalysts is a coke deposition on the catalysts, which leads to catalyst deactivation. As a solution, we paid attention to Cr species interacting with zeolites because our previous work revealed that the Cr species improved the coke deposition resistance [2]. Herein, we impregnated Ni and Cr on a dealuminated Beta zeolite and investigated the effect of Cr on the amount of coke deposition after DRM reactions.

Experimental/methodology. The dealumination process was achieved by treating commercial Beta with 35 wt% nitric acid (the mass ratio of nitric acid and zeolite was 10:1) at 393 K for 24 h. The resultant powder was washed with deionized water. After drying at 363 K, the powder was calcined at static under air at 823 K for 5 h. The dealuminated Beta was impregnated with an aqueous solution of $Cr(CH_3COO)_3$, containing the amount of chromium needed to obtain the desired chromium content in the samples (Cr(x)/deAl-Beta), where x means the mass content of Cr_2O_3. After impregnation, the samples were dried at 363 K and calcined under air at 823 K for 5 h. The Cr(x)/deAl-Beta was impregnated with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ similarly with the impregnation of Cr. The obtained samples were donated as Ni/Cr(x)/deAl-Beta. As a comparison, the only Ni-loaded sample without Cr (Ni/deAl-Beta) was prepared by a similar impregnation method using dealuminated Beta and an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$. DRM reactions were carried out at 873 K for 5 h under the mixed gases flow of CO_2 and CH_4 (v : v =1 : 1) with a total flow rate of 40 sccm using 0.05 g of catalysts. The amounts of carbon deposition for spent catalysts were analyzed by TGA.

Results and discussion. No significant decrease in CO yield was observed by adding Cr. We summarized the amount of coke deposition for spent catalysts in Fig. 1. The spent Ni/deAl-Beta catalyst has the highest coke deposition (286 %). In contrast, coke deposition was lower for the Cr-doped samples. Furthermore, in the Ni/Cr(2.0)/deAl-Beta, the smallest amount of deposited coke was observed (1.1 %). XRD measurements confirmed the *BEA-type derived peaks in all synthesized samples. These samples showed a shift in the peaks which are characteristic of *BEA-type zeolite compared to the commercial beta. From UV-vis spectra, peaks derived from Cr (VI) were detected in all Cr-doped samples. These results suggest that Cr (VI) in the framework of dealuminated Beta contributed to the suppression of coke deposition in the DRM reaction.

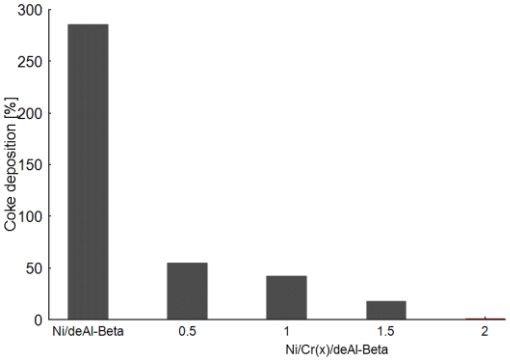

Fig. 1 The amount of coke deposition for spent catalysts.

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Layered Double Hydroxides based catalytic systems for photoelectrochemical CO_2 conversion into solar fuels and chemicals

E. Tosi Brandi[1,3], E. Orfei[1,3], A. Fasolini[1,3], N. Sangiorgi[2], A. Sangiorgi[2], A. Sanson[2], F. Basile[1,3]

[1] *Industrial Chemistry Department "Toso Montanari", University of Bologna, Bologna, Italy.*
[2] *Institute of Science and Technology for Ceramics, National Research Council (ISTEC-CNR), Faenza, Italy.*
[3] *Center for Chemical Catalysis - C3, University of Bologna, Bologna, Italy*
**eleonora.tosibrandi2@unibo.it*

Keywords: CO_2 conversion, Photo-Electrocatalysis, Layered Double Hydroxides, solar fuels

Introduction

Photoelectrochemical CO_2 valorization is a sustainable and promising way to reduce carbon dioxide concentration in atmosphere through its capture and conversion into fuels and chemicals. Tremendous efforts have been already made to identify the best materials and device configuration for efficient CO_2 reduction reaction (CO_2RR) in Photoelectrochemical Cell devices (PEC) [1]. Layered Double Hydroxides (LDHs) anionic clays represent an appealing option for such application thanks to their good affinity for CO_2 and tunable chemical composition [2]. This aspect allows to modify morphological, physical-chemical, and electrochemical properties of the material to provide good catalytic activity.

Experimental/methodology

Ni, Cu and Fe containing LDHs films supported on a conductive glassy substrate (FTO) were produced through screen printing deposition of LDH powder-based ink. Bulk LDHs have been synthetized by coprecipitation method as described in a previous work of our group [3]. The photoelectrodes have been characterized with different techniques (XRD, SEM, UV-Vis, cyclic voltammetry (CV), Linear Sweep Voltammetry (LSV), Electrochemical Impedance Spectroscopy (EIS) and Mott-Schottky analysis. Photoelectrocatalytic CO_2 reduction tests were performed in a three-electrodes PEC cell equipped with a quartz window.

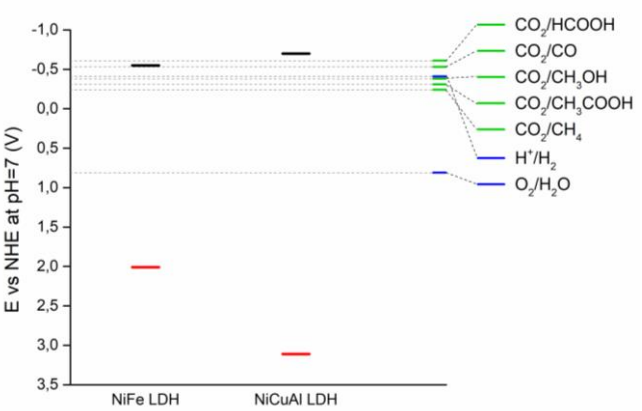

Figure 1 - Band-edge positions of samples based on LDHs relative to standard potential of CO_2RR of interest for solar fuels production.

Results and discussion

XRD and SEM analysis underlined the morphological homogeneity of the samples, both powder and films, as well as the presence of the desired LDH phase. Band gap and electronic energy levels' position of the samples have been defined and confirmed compatible with standard potentials of CO_2RR thanks to UV-vis DRS and Mott-Schottky tests respectively (Figure 1). The characterization of the electron transfer ability, charge accumulation capability, and materials conductivity of the LDHs by CV, EIS and LSV showed that both NiFe 3:1 LDH and NiCuAl 3:1 LDHs provided an appreciable cathodic current density starting at -1.25 V vs Ag/AgCl, resulting promising materials for PEC electrodes. Furthermore, the film based on NiCuAl LDH showed a good adherence to the substrate and fast charge mobility as well as a lower resistance towards charge transfer at the electrode/electrolyte interface.

These properties were linked to the photoelectrocatalytic activity. Indeed Ni, Cu, Fe containing LDHs demonstrated to be active in photoelectrochemical CO_2RR with higher selectivity for C-containing products i.e., formic and acetic acid, over hydrogen evolution at relatively low potential of – 0.8 V vs NHE (pH=7), while H_2 production was the favored when higher potential was applied i.e., – 1.3 V vs NHE (pH=7).

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Influence of pre-treatment on the support effect in catalytic methanol synthesis

J. A. Boysen[1], A. D. Jensen[1], J. M. Christensen[1*]

[1]*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads 228A, Kgs. Lyngby, Denmark*

[*]*jmc@kt.dtu.dk*

Introduction. Methanol as an energy vector has experienced increasing interest due to the possibility to produce CO_2-neutral methanol from captured CO_2 and H_2 generated from electrolysis using sustainable electricity. This way it is possible to reduce CO_2 emissions related to conventional methanol production based on fossil feedstocks.
For Cu-catalyzed hydrogenation of CO_2 to methanol, the reaction rate and the Cu surface area are linearly correlated [1], which indicates that the reaction occurs on the Cu surface. However, the industrially applied ZnO-support raises the turnover frequency per Cu surface atom by an order of magnitude and this essential metal-support synergy is not fully understood. Kuld et al. [2] found that H_2 pre-treatment of a $Cu/ZnO/Al_2O_3$ catalyst accelerated the reaction rate and suggested Zn-Cu surface alloy formation as the cause of this effect. This proposal seems to be at odds with the observation that metallic Zn is found to be oxidized in CO_2-containing reaction gas [3-4]. The aim of this work is to enhance the understanding of the active site of the industrial $Cu/ZnO/Al_2O_3$ catalyst by investigating how the catalyst is affected by pre-treatments with CO or H_2.

Experimental/methodology. The $Cu/ZnO/Al_2O_3$ catalyst was prepared by co-precipitation from metal nitrate precursors and sodium carbonate as the precipitating agent at T = 65 °C and pH = 6.5, followed by drying overnight at around 50 °C and calcination at 330 °C. The catalyst is loaded in a flow reactor setup described elsewhere [5]. The catalyst was then subjected to pre-reduction (with either 5 % H_2/N_2 or 10% CO/Ar) followed by a pre-treatment in different H_2 partial pressures. Raney Cu (referred to as pure Cu without support) was tested similarly to study the effect without support interactions. The pre-treated catalyst was tested in methanol synthesis using a synthesis gas flow rate of 200 NmL/min with a composition of H_2/CO_2 = 80/20 at 135 °C and a pressure of 1 atm. Additionally, TPD experiments, N_2O adosprtion and infrared spectroscopy were conducted to determine the amount of adsorbed H_2, Cu surface area and to study how the catalysts and adsorbates are affected by the pre-treatment, respectively.

Results and discussion. Figure 1 illustrates that the pre-reduction atmosphere has a major impact on the catalytic activity. Pre-treatment of the reduced catalyst with varying H_2 pressures prior to catalytic tests show a beneficial effect on the methanol reaction rate. However, this effect is not primarily due to a reduction of the support, since pre-reduction in a more reducing gas (CO vs H_2) leads to an inferior catalytic performance (see Figure 1). The reasons behind these effects are elucidated from catalytic and spectroscopic investigations.

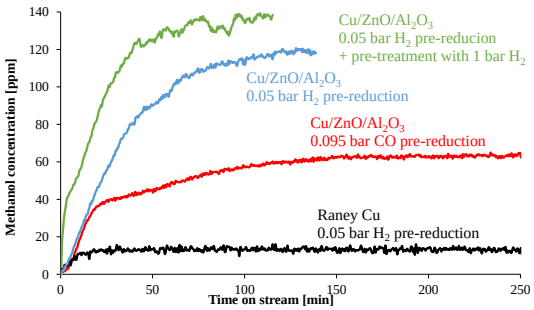

Figure 11 The methanol effluent concentration as a function of time on stream at H_2/CO_2 = 4/1, 135 °C, 1 atm for differently pre-treated catalysts.

Acknowledgments

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Development of multi-elemental reverse water-gas shift catalysts using extrapolative machine learning approach

D. Chen,[1] G. Wang,[1] S. Mine,[1] I. Takigawa,[2,3] K. Matsushita,[4] K. Shimizu,[1*] T. Toyao[1*]

[1]*Institute for Catalysis, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan*
[2]*RIKEN Center for Advanced Intelligence Project, 1-4-1 Nihonbashi, Chuo-ku, Tokyo 103-0027, Japan*
[3]*WPI-ICReDD, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan*
[4]*Central Technical Research Laboratory, ENEOS Corporation, Yokohama 231-0815, Japan*
[*] *toyao@cat.hokudai.ac.jp, kshimizu@cat.hokudai.ac.jp*

Keywords: machine learning, CO_2 hydrogenation, reverse water-gas shift, catalysis informatics

Introduction.

Recent revolution in data science could significantly accelerate the pace of new catalyst development and greatly impact the on-going catalysis research.[1] Machine learning (ML), a sub-field of data science, would play a central role in this paradigm shift. Despite having already seen proof-of-concept examples that artificial intelligence (AI) can reduce the time and costs involved in catalyst development, most research has been directed toward the resolution of benchmark problems, but truly novel compounds and materials have rarely been discovered. This is due to one of the most common limitations of ML—an assumed inability for models to extrapolate, i.e. to identify extraordinary materials beyond those present in the training data set. In materials and catalysis informatics, we often desire to use ML models to find entirely new classes of materials and catalysts, with heretofore-unseen combinations of elements.

In this context, our group has developed a new ML approach that uses elemental features as the input representations, rather than inputting the catalyst compositions directly.[2-4] In our method, the elemental composition ratios are multiplied by elemental descriptors such as electronegativity and atomic radius, which are unique for each element. This ML method has the potential to guide catalyst design and discovery in areas where limited catalyst composition overlap exists, even for elements previously unseen in the given dataset. This will enable us to make extrapolative prediction beyond the training data.

Results and discussion.

In this study, we have applied this ML approach to develop multi-elemental catalysts based on supported Pt as an active metal and TiO_2 as a support for the reverse water-gas shift (RWGS) reaction.[5] Our ML model efficiently spot active catalyst candidates with high predictive accuracy and identified multi-elemental catalysts which exhibited the best CO formation rates compared to any reported RWGS performances at $T \leq 250$ °C with 100% CO selectivity. The composition of the most optimal catalyst discovered by this approach was Pt(3)/Rb-Ba-Mo-Nb/TiO_2. Notably, Nb was not included in the original dataset, and the catalyst composition identified would be hardly predictable even by human experts.

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Plasma-catalytic CO_2 hydrogenation over a Pd/ZnO catalyst: Insights into gas-phase and surface reactions

Y. Sun[1], Y. Wang[2], D. Ye[1], X. Tu[2*]

[1]*School of Environment and Energy, South China University of Technology, Guangzhou, China*
[2]*Department of Electrical Engineering and Electronics, University of Liverpool, Liverpool, UK*
[*]*xin.tu@liverpool.ac.uk*

Keywords: Non-thermal plasma, Plasma catalysis, CO_2 hydrogenation

Introduction

CO_2 hydrogenation to CO, also called the reverse water gas shift (RWGS) reaction, has received increasing interest recently, especially in conjunction with the Fischer-Tropsch process to produce hydrocarbon fuels. However, RWGS is endothermic and thus is thermodynamically favorable at higher temperatures. Non-thermal plasma (NTP) is an emerging technology for CO_2 valorization under mild conditions [1-3]. In addition, coupling NTP with catalysis (plasma catalysis), has great potential to create a synergistic effect due to plasma-catalyst interactions [4], offering an effective way for the selective production of chemicals and fuels from CO_2. However, plasma-catalytic chemical reactions (*e.g.*, CO_2 hydrogenation) are a complex chemical process. The exact reaction pathways in the plasma-catalytic CO_2 hydrogenation have not been fully explored, particularly the plasma-assisted reactions on surface of the catalyst. In this work, the plasma-catalytic hydrogenation of CO_2 over ZnO and Pd/ZnO was investigated using *In situ* plasma/FTIR combined with online MS and OES analysis to understannd plasma-assisted gas-phase and surface reactions.

Experimental/methodology

Plasma-catalytic CO_2 hydrogenation was conducted in a dielectric barrier discharge (DBD) plasma reactor. A mixture of H_2 and CO_2 with an H_2/CO_2 ratio of 3:1 was used. The catalyst (0.5 g) was packed into the entire discharge gap and was reduced by H_2/Ar mixed gas (H_2/Ar = 1:9) at 400 ^oC for 4 h before the reaction. All the electrical signals were recorded using an oscilloscope (Tektronix DPO 3034).

Results and discussion

The conversion of CO_2 and H_2 was 21.3% and 9.3%, respectively, in the plasma reaction with no packing. However, placing ZnO in the DBD did not enhance the conversion of CO_2 (20.2%) and H_2 (8.4%). In contrast, the combination of DBD with 2 wt.% Pd/ZnO notably improved the conversion of CO_2 and H_2 to 36.7% and 16.9%, respectively. Moreover, in comparison to the plasma only system, the incorporation of plasma with ZnO or Pd/ZnO showed a similar CO selectivity (93.2-96.6%). *In situ* spectroscopy techniques including *in situ* FTIR, online MS and OES diagnostics combined with catalyst characterization and kinetic analysis were used to understand the role of Pd/ZnO in the plasma-catalytic CO_2 hydrogenation. In the plasma-catalytic reaction using Pd/ZnO, the hydrogenation of adsorbed CO_2 on Pd/ZnO significantly contributes to the enhanced CO_2 conversion, which can be attributed to the formation of a ZnO_x overlay as a consequence of the SMSI between ZnO and Pd, and the presence of abundant H species (evidenced by plasma-assisted H_2-TPD analysis) on the Pd/ZnO surface due to H_2 activation by Pd NPs. However, without Pd loading, the hydrogenation of surface adsorbed CO_2 on the ZnO surface was limited due to the absence of the SMSI and the lack of active H species formed on the ZnO surface. The splitting of CO_2 to CO is believed to make major contributions to the conversion of CO_2, in both the gas phase and on the ZnO surface during the plasma-catalytic CO_2 hydrogenation over ZnO. This work provides new insights into the reaction pathways for plasma-catalytic chemical reactions, particularly plasma-assisted surface reactions.

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CO_2 Adsorption on the Modified Mesoporous Silicas

Oyundari Tumurbaatar[1*], Margarita Popova[1], Violeta Mitova[2], Pavletta Shestakova[2] and Neli Koseva[2]

[1]Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., bl. 9, 1113 Sofia, Bulgaria;
[2]Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St., bl. 103A, 1113 Sofia, Bulgaria;
[*]Corresponding Author's E-mail address: Oyundari.Tumurbaatar@orgchm.bas.bg

Keywords: CO_2 capture, modified mesoporous silicas, DOPO derivative

Introduction. The large amounts of carbon dioxide released into the atmosphere by human activities (greenhouse effect) is considered one of the great challenges of the twenty-first century [1]. Therefore, the CO_2 controlling emission, capture, and recycling attract worldwide attention, which reveals a strong prospect for greenhouse level decrease. The adsorption approach is one of the most promising methods due to its high selectivity and low energy penalties [2]. The mesoporous silica materials are widely studied sorbents. They possess a large number of silanol groups, which is a key precondition for suitable functionalization with different organic molecules, which improve silica's performance in CO_2 adsorption. Mesoporous silicas are extensively used for amine immobilization by covalent bonds [3] or hydrogen bonds [4] and used for CO_2 capture and separation due to the large pore volume, and high specific surface area.

In this study, mesoporous KIT-6, SBA-15, and SBA-16 silicas modified with DOPO derivative (DAPTES)-were developed and studied as efficient adsorbents of CO_2.

Experimental/methodology. KIT-6, SBA-15, and SBA-16 were prepared by hydrothermal synthesis. The post-synthesis procedure for DAPTES-modified mesoporous KIT-6, SBA-15, and SBA-16 silicas was developed. The materials were characterized by NMR spectroscopy, ATR-FTIR spectroscopy, N_2 physisorption. CO_2 adsorption experiments were performed in dynamic and equilibrium conditions.

Results and discussion. The DAPTES-modified mesoporous silicas with different pore structures, 2D SBA-15 and 3D SBA-16, and KIT-6, were successfully synthesized by a simple two-step post-synthesis procedure. The preservation of mesoporous structure during the modification procedure was detected for the obtained new mesoporous materials. Higher capacity for CO_2 adsorption was determined for all modified materials depending on the structural peculiarities of the supports used in comparison to the initial ones. The higher CO_2 adsorption capacities were detected for DAPTES-modified silicas in the experiments with 3 vol.% CO_2 plus 1 vol.% water vapor due to the facilitated formation of chemisorbed CO_2 in the form of a bicarbonate ion (HO-COO-) in the presence of water as well as the presence of physisorbed CO_2. The chemisorption of CO_2 for DAPTES-modified silicas was assumed based on the calculated heats of adsorption for the studied materials. The DAPTES-modified mesoporous SBA-15 silica showed the highest adsorption capacity for CO_2 (3.9 mmol/g). The total CO_2 desorption from the modified materials was achieved at 80°C.

Acknowledgments

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Kinetic and mechanistic study of CO_2 conversion into methanol over Cu/TiO_2 and Cu/SiO_2 catalysts promoted by CeO_2

Tomás Vergara[1], Daniel Gómez[1], Bruno Lacerda de Oliveira Campos[2], Karla Herrera-Delgado[2], Patricia Concepción[3], Romel Jiménez[1], Alejandro Karelovic[1,*]

[1]*Laboratorio de Carbono y Catálisis, Universidad de Concepción, Concepción, Chile*
[2]*Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Karlsruhe, Germany*
[3]*Instituto de Tecnología Química, Universidad Politécnica de Valencia, Valencia, Spain*
[*]*akarelov@udec.cl*

Keywords: Methanol, CO_2 hydrogenation, *operando* - DRIFTS, SSITKA, CeO_2

Introduction. At present, there is no consensus about the reaction mechanism for the formation of methanol from CO_2 on Cu catalysts promoted by CeO_2. On one hand, there are authors who propose that the interfacial site between Cu and Ce is able to adsorb CO_2 and make it react towards methanol at a high rate [1]. A second group claims that CeO_2 would have no effect and that Cu/CeO_2 catalysts are kinetically equivalent to Cu/SiO_2 [2]. This study focuses on elucidating the reaction mechanism of the CO_2 hydrogenation on Cu-based catalysts promoted by CeO_2, as well as the structural and kinetic effect of TiO_2.

Experimental/methodology. $CuCeO_x/TiO_2$ and $CuCeO_x/SiO_2$ (6% wt. Cu) catalysts were synthesized by wetness impregnation with different Ce/(Cu + Ce) molar ratios. The catalytic activity was measured in a fixed bed reactor at 8, 30 and 50 bar. Catalysts were characterized through XRD, *quasi-in situ* XPS, TEM, CO adsorption and H_2-TPR. *Operando* – DRIFTS, H_2/D_2 isotopic exchange, product feeding, KIE (D_2/H_2) and DRIFTS/MS – SSITKA ($^{12}CO_2/^{13}CO_2$) analyzes were carried out.

Results and discussion. The characterizations showed that TiO_2 improves the dispersion of Cu and evidenced a SMSI between Cu and TiO_2. CeO_2 promotes methanol synthesis, which is important for low CeO_2 concentrations and shows an asymptotic behavior in terms of the apparent activation energy (figure 1-a) and other parameters (CH_3OH rate, conversion, apparent reaction order). This behavior occurred regardless of the support and pressure, and it is attributed to the generation of a new interfacial active site between Cu and CeO_2 and the formation of a greater number of sites for higher promoter concentrations. It was evidenced that the production of CO is sensitive to the catalyst support while CH_3OH is independent of it (figure 1-a). Indeed, TiO_2 increases methanol selectivity by inhibiting the formation of CO. Consistently, it is suggested that the active site for CO would be the copper surface and, due to the SMSI, these sites would be affected by TiO_2. The spectroscopic and DRIFTS/MS – SSITKA studies allowed to clarify that (i) formates are the main intermediates in the methanol pathway (figure 1-b), (ii) there are formates adsorbed on copper (spectators) and interfacial sites (active) (figure 1-b) and (iii) CO would be synthetized assisted by hydrogen, likely via carboxyl. From this, a consistent macrokinetic model was derived.

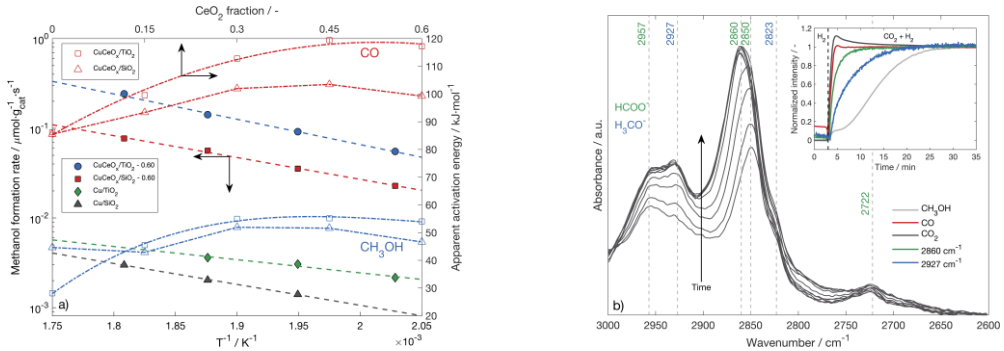

Figure 1. a) Arrhenius plot for 4 different catalysts (P = 8 bar, 20 mL/min) and apparent activation energy as a function of CeO_2 content and support. b) *operando* – DRIFTS over $CuCeO_x/TiO_2$ – 0.60 following the switch 20%CO_2/60%H_2 →20%He/60%H_2, P = 6 bar, T = 240°C, 25 mL/min.

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Supported metal oxide materials for plasma-catalytic dry reforming of methane

Valeria Vermile[1*], Sander Bossier[1], Bram Seynnaeve[2], Jeroen Lauwaert[2], An Verberckmoes[2], Vera Meynen[1]

[1]*University of Antwerp, Wilrijk, Belgium*
[2]*Ghent University, Ghent, Belgium*
[*]*Valeria.Vermile@uantwerpen.be*

Keywords: plasma catalysis, dry reforming of methane, CO_2 conversion, dielectric barrier discharge.

Plasma catalysis is gaining increasing interest for various gas conversion applications, such as CO_2 conversion into value-added chemicals and fuels, CH_4 activation into hydrogen, higher hydrocarbons or oxygenates, and NH_3 synthesis [1]. Plasma is an electrical energy driven process, important for the worldwide transition to renewable energy. Its highly energetic, collision-rich environment, is able to activate relatively stable compounds at milder and more convenient conditions (ambient pressure and near ambient temperature) than for classical thermal processes [2]. However, plasma catalysts currently have the drawback of not being selective and still requiring progress in energy efficiency. The interactions between plasma and catalyst are complex as the chemical and physical properties of both can be modified by the presence of each other. The catalyst influences the plasma characteristics in a physical way (e.g., through changes in electric field, discharge, sorption processes), and this has an impact not only on selectivity, but also on conversion [3]. The key challenge is then to design cost-effective, highly active, selective and stable catalysts tailored to the plasma environment.

In this context, we evaluate the impact of different spherical γ-alumina packing materials activated with different metal oxides (10%) on dry reforming of methane (DRM) to understand the influence of the metal oxide deposited on selectivity and conversion. The reaction was performed in a packed bed DBD (dielectric barrier discharge) plasma reactor with a 4.44 mm discharge gap size, setting the experimental conditions at 15 W, 3 kHz and a residence time of 40 s. All catalysts were synthesized using a dry impregnation procedure [4]. γ-Al_2O_3 microspheres with a diameter of 1.8 mm were used as support and different metal oxides were selected as active elements. The catalysts were dried by removing water overnight under vacuum at 150°C. The CO_2, CH_4 and total conversion are clearly influenced by the presence of metal oxides on the γ-Al_2O_3 surface. Interesting results have been obtained regarding the selectivity of the different materials.

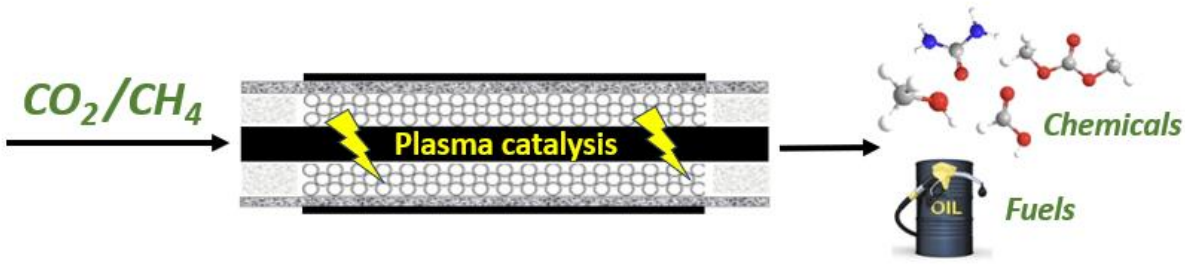

Figure 1. Plasma catalysis for CO_2 and CH_4 conversion into liquid fuels and chemicals.

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Alternative production path of reverse water-gas shift catalysts via solution combustion synthesis

N. Virkki[1*], C. Alvarez[2], P. Simell[3], J. Kihlman[4]

[1]*VTT, Espoo, Finland*
[2]*CSIC, Madrid, Spain*
[3]*VTT, Espoo, Finland*
[4]*VTT, Espoo, Finland*
[*]*niko.virkki@vtt.fi*

Keywords: Solution combustion synthesis, reverse water-gas shift, Fischer-Tropsch

Introduction. In a hope to contain the negative effects of the climate change several technologies are being developed to capture carbon dioxide and use it as a feedstock for synthethic fuels and other useful value added chemicals [1]. One of the key reactions in CO2 activation is reverse water-gas shift reaction (RWGS). This reaction can be utilized effectively to convert carbon carbon dioxide to synthesis gas, which is a key feedstock for the Fischer-Tropsch (FT) process for hydrocarbon production [2].

In this study solution combustion synthesis (SCS) will be used to produce catalysts for RWGS reaction. Laboratory scale tests will be conducted with the SCS catalysts to determine if there is an advantage in SCS catalysts versus traditional conformated active metal catalysts in activity, adsorption, resistance to deactivation or applicability for interesting reactor geometries such as microchannels or metallic substrates. The SCS method is energy and time efficient way to produce porous nano powders that do not suffer from non-uniformity as the self sustaining exothermic reaction produces thermodynamically favourable shapes [2].

Experimental/methodology. The SCS method is based on self-sustained exothermic reactions that produce highly porous materials [2]. The method utilizes a fuel, usually an organic such as glycine or urea, and an oxidizer in the form of metallic nitrates [2], that in our case also contain the active metals of the catalyst that is produced. The fuel and the oxidizer are heated in an aqueous solution to 100-200 ^{o}C until the water has evaporated and the dry reactants heat further and start the reaction [3]. The SCS catalyst is tested with RWGS reaction in powdered form as well as coated on substrates. The results of the powdered SCS catalysts made at CSIC are compared to conformated catalysts made at VTT.

Catalyst testing is done with bottled reactant gases (CO2 and H2) that are fed into a reactor heated with an oven. Reaction products and the unreacted gases are analyzed with gas chromatographs and online gas analyzers in order to calculate the mass balances and conversion.

Results and discussion. The experiments are ongoing so the results will be released at the Europacat2023 seminar. The results of this work will deepen the understanding of the effect of the highly porous structure of the SCS catalyst powder on the RWGS reaction. The data will be used for scaling a pilot sized RWGS reactor coupled to a FT unit called mobile synthesis unit (MOBSU).

Acknowledgments
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Non-thermal plasma catalytic CO_2 hydrogenation to methanol at atomospheric pressure

Shanshan Xu[1,*], Andrew M. Beale[2,3], Raquel Simancas[4], Matthew E. Potter[2,3], Sofia Mediavilla Madrigal[3,5], Toru Wakihara[4], Xiaolei Fan[1], Christopher Hardacre[1,*]

[1]*Department of Chemical Engineering, The University of Manchester, Oxford Road, Manchester M13 9PL, UK*

[2]*Department of Chemistry, University College London, 20 Gower St, WC1H 0AJ, London, UK*

[3]*Research Complex at Harwell, Rutherford Appleton Laboratory, OX11 0FA, Harwell, Didcot, UK*

[4]*Institute of Engineering Innovation, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 3-8656, Japan*

[5]*School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK*

Keywords: non-thermal plasma, CO_2 hydrogenation, methanol

Introduction. CO_2 hydrogenation to methanol is a promising process for CO_2 utilization for a sustainable carbon recycling process. Conventional thermocatalytic conditions for this process are energy intensive, requiring high temperatures (200-300 °C), and high pressures (30-100 bar) to form methanol [1]. In contrast, non-thermal plasma can activate CO_2 effectively under mild conditions (e.g., room temperature and atmospheric pressure) [2]. However, the synergistic effects between plasma and catalysts, the nature of the active species and the mechanistic understanding of CO_2 hydrogenation in plasma catalysis are still lacking. In this work, we focus on CO_2 hydrogenation into methanol at room temperature and atmospheric pressure by using plasma catalysis over ZSM-5 zeolite supported Cu and CuZn catalysts. we have shown that comparing Cu catalyst, CuZn-based catalysts have a promoting effect on the methanol formation under plasma conditions.

Experimental/methodology. The catalytic activity, selectivity and stability of the developed catalysts were assessed in a dielectric barrier discharge flow reactor. Aluminium foil was wrapped around outside of the quartz tube was used as the high voltage electrode, while a stainless-steel rod placed in the centre of the quartz tube was used as the ground electrode. The outlet gas composition was analysed by a two-channel on-line gas chromatography.

Results and discussion. For Cu/ZSM-5 catalyst, highest CO_2 conversion of 12% with a 18% methanol selectivity was achieved at NTP power of 2.5W. This demonstrated that NTP catalysis can form methanol at atmospheric pressure and room temperature. Comparatively, the NTP system using the packing of CuZn catalysts showed the higher CO_2 conversions and selectivity to methanol regardless of plasma energy, indicating that Zn addition promoted CO_2 conversions to methanol. For example, the CuZn/ZSM-5 (Cu/Zn=1) catalyst showed the higher activity with the highest CO_2 conversion of 14.5% and selectivity of methanol of 36% achieved at power of 2.5 W. H_2-TPR and CO_2-TPD showed that Zn addition improved the reductivity of Cu and affect the CO_2-Cu interactions, which may affect the catalytic performance for CO_2 hydrogenation. Additionally, in situ DRIFTS for CO_2 hydrogenation over Cu/ZSM-5 and CuZn/ZSM-5 catalysts shows similar active intermediates for methanol, indicating that Zn addition did not affect the pathway for CO_2 hydrogenation to methanol.

Acknowledgments

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Analysis of photocatalytic CO_2 reduction by machine learning

Dilara Saadetnejad, Burcu Oral, Elif Can, Ramazan Yıldırım*

Boğaziçi Univeristy, Istanbul, Turkey
**yildirra@boun.edu.tr*

Keywords: Photocatalytic CO_2 reduction, Band gap prediction, Machine learning

Introduction.

Methane and CO_2 are considered as effective greenhouse gases causing global warming. It is important to reduce the CO_2 emission or to utilize CO_2 more effectively to decrease the adverse effects on climate. Reducing CO_2 by photocatalysis is a cost-effective way to convert CO_2 into valuable products since it uses solar energy. Methanol, methane, carbon monoxide, and hydrogen are the main products in CO_2 photoreduction, whereas formic acid, formaldehyde, ethanol, acetic acid, acetaldehyde, ethylene, and ethane may also be produced. This work analyses gas and liquid-phase photocatalytic CO_2 reduction using machine learning. The band gap of the photocatalysts and the total gas production rate were predicted using random forest and decision tree algorithms.

Experimental/methodology.

The dataset for liquid and gas phase CO_2 reduction was collected from 80 articles that were published between 1993-2019. There were 549 data points of which 268 cases were for the gas phase and 281 cases for liquid phase processes. The collected input variables (total of 21) included details about the semiconductor, co-catalyst, their preparation methods, and operation conditions. Train-test split ratio of 80-20% was determined to be optimum and hyperparameter tuning of algorithms was done using five-fold cross-validation. Random forest algorithm was used to predict band gap values of missing cases. The minimum number of instances in a terminal node (*nodesize*) and the number of trees (*ntree*) were used as hyperparameters, and the optimum values were found to be 5 and 75 respectively. Decision tree clasification was used to predict the conditions leading low and high gas production rates. *Minsplit* and *complexity parameter* were chosen as hyperparameters and optimum values were found to be seven and 0.01 respectively.

Results and discussion.

The descriptive analysis of the dataset showed that the main products of the gas phase are H_2, CO, and CH_4 while CH_3OH production is more dominant in the liquid phase. The hydrogen production in the gas phase is higher under visible light and also CO production is favored. The most commonly used semiconductor is TiO_2 followed by C_3N_4 and CdS; the most frequently used co-catalysts are Cu, Ag and Pt. The random forest model for band gap prediction had high prediction power with RMSE of 0.12 and 0.15 for train and test sets respectively. [Figure 1) Decision tree models for the total gas production rates were also successful; 80% and 79% accuracies were achieved for training and testing respectively for the gas phase process.

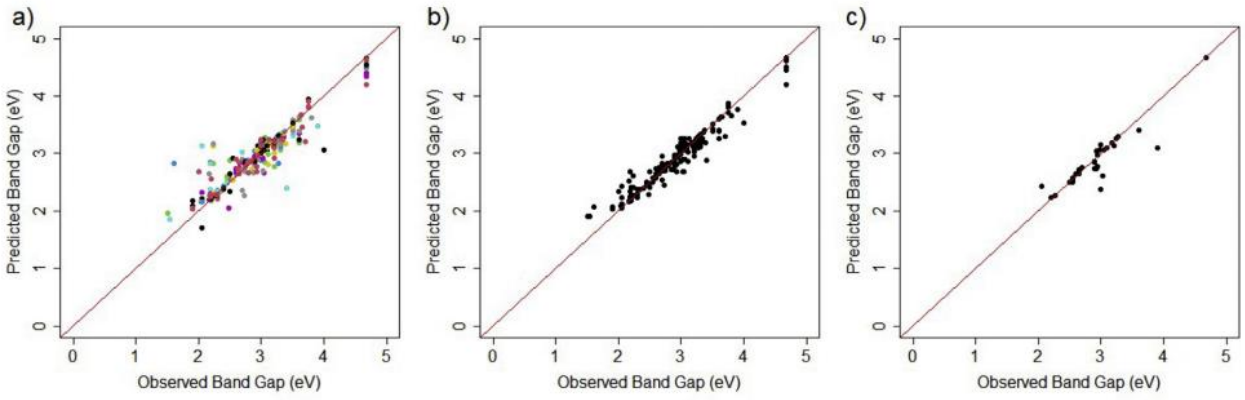

Figure 1. Random Forest prediction results for a)validation b)train and c)test set for band gap values

for preparation methods b)Decision tree heuristics for band gap classes

Analysis of Catalytic CO_2 Methanation by Machine Learning

B. Yılmaz, B. Oral, R. Yıldırım*

Boğaziçi University, Department of Chemical Engineering, Istanbul, Türkiye
**yildirra@boun.edu.tr*

Keywords: Catalytic CO_2 methanation, Machine learning, Random forest, CO_2 conversion prediction

Introduction. Carbon dioxide is a major greenhouse gas that causes global warming. Great efforts have been made to diminish CO_2 emissions generated by industry [1]. Catalytic CO_2 methanation process is one of the promising solutions which constitute a route to eliminate CO_2 release into atmosphere by converting it to valuable energy carrier CH_4 [2]. Methanation, discovered by Sabatier in 1902, includes the following catalytic reactions in the presence of excess H_2[3].

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta H_{298K} = -165\ \text{kJ mol}^{-1} \qquad (1)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H_{298K} = -206\ \text{kJ mol}^{-1} \qquad (2)$$

CO_2 is a highly stable compound which needs high temperatures to be activated although the Sabatier reactions are favored in ambient conditions [4]. Hence, the challenge of methanation process is to identify optimum operating conditions and proper catalysts for high yield and selectivity for methane [5]. In this context, numerous studies have been performed to design catalysts with high activity at optimum conditions. As a result, a good deal of experimental data has been accumulated in methanation literature, which can be analyzed by machine learning tools to find a reliable pathway that leads to high CO_2 conversion to methane.

The aim of this work is to extract knowledge on the catalytic CO_2 methanation from published articles in literature and to predict the CO_2 conversion. The significant variables were identified by Boruta analysis and the predictive model for CO_2 conversion was developed using random forest algorithm.

Experimental/methodology. CO_2 methanation dataset, consists of 4051 data points from 527 distinct experiments, was created using 100 papers that were published between 2011-2022. There were 23 descriptors related to catalyst contents, preparation methods, and reaction conditions. The data was split into training (80%) and testing (20%). The 5-fold cross validation procedure was used for hyperparameter optimization. Random forest algorithm was used to predict CO_2 conversion, and Boruta analysis was performed to determine the significant variables. The optimum values for the number of trees (ntree) and the minimum number of instances in a terminal node (nodesize) were found to be 220 and 5 respectively.

Results and discussion. The random forest model successfully predicted the CO_2 conversion with the training and testing root mean square error (RMSE) of 6.4 and 12.7 respectively; R^2 was 0.95 for training and 0.87 for testing (Figure 1). The validation procedure was also performed succesfully by employing the model to obtain CO_2 conversion values with respect to operating temperatures for each experiment in test data and comparing them with the experimental data reported in publications. Reaction temperature was identified as the most significant variable in CO_2 conversion prediction, while the catalyst properties such as support type, preparation method, metal loading, and metal base type were also important in CO_2 conversion.

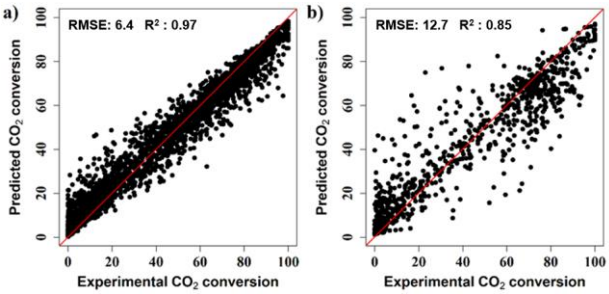

Figure 1. Predicted vs real conversion results from random forest model for a) training b) testing sets.

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Template-free synthesis of mesoporous amine-bridged organosilicas for CO_2 valorization into cyclic carbonates

T. Q. Bui*, Z. Moravec, P. Machac, A. Styskalik

Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic
**Corresponding Author: 247831@mail.muni.cz*

Keywords: mesoporous amine-bridged organosilica, non-hydrolytic sol-gel, CO_2 utilization, cyclic carbonate

Introduction.

Synthesis of cyclic carbonates from CO_2 and epoxides using heterogeneous catalysts is one of the most promising routes for chemical fixation of CO_2 on industrial scale due to 100% atom economy and ease of product separation. Mesoporous amine-functionalized silicas could act as potential catalytic materials for this reaction as they are low-cost and enable high accessibility of active Lewis basic N-sites for CO_2 activation [1]. In addition, these solid amines are well-known in CO_2 capture and utilization studies due to their high CO_2 selectivity and uptake even at low CO_2 concentration as in ambient air [2,3].

Experimental/methodology.

Herein, we report a template-free, one-pot preparation of mesoporous amine-bridged organosilicas via non-hydrolytic sol-gel reactions between 2 silicon precursors ($SiCl_4$, $Si(OAc)_4$) and 4 aminosilane precursors (3-aminopropyl)trimethoxysilane, bis[3-(trimethoxysilyl)propyl]amine, bis[3-(trimethoxysilyl)propyl]-N-methylamine, tris[3-(trimethoxysilyl)propyl]amine (denoted as N1, N2, N3-methyl and N3, respectively) in dry CH_2Cl_2/THF/toluene at 140-180 °C for 4 days. The obtained gels were dried under vacuum at 120 °C overnight. The structure and surface chemistry of these xerogels were characterized mostly by means of solid-state NMR spectroscopy and XPS. The textural properties were characterized by N_2 sorption at 77 K while the CO_2 uptakes and the heat of adsorptions were characterized by CO_2 sorptions at 273 K and 298 K. The catalytic reactions between CO_2 and epoxides (epichlorohydrin, 1,2-butylene oxide, styrene oxide) were performed in batch reactor under solvent-free and co-catalyst-free conditions at 120 °C and 10 bar of initial CO_2. Reaction mixtures were analyzed by NMR (in $CDCl_3$) and GC-MS. Reusability tests of catalysts were also performed. The spent catalysts were also characterized and discussed.

Results and discussion.

The obtained N-containing xerogels are mostly mesoporous with large specific surface areas and pore volumes (Table 1). Xerogels obtained from combinations between bridged aminosilanes and $Si(OAc)_4$ in toluene achieve excellent porosity and structural integrity (i.e., no side reactions during condensation, only expected signals in MAS NMR spectra). The catalytic performance of prepared highly porous materials depends mostly on the structure of amine sites with tertiary and non-sterically-congested amine site being the most active (Table 1).

Table 1. Preliminary results of xerogels obtained from combinations between aminosilanes and $Si(OAc)_4$ in toluene at 180 °C for 4 days

xerogel	aminosilane	SSA_{BET} ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	PS_{DFT} (nm)	conversion* (%)
1	N1	non porous			11
2	N2	624	1.32	7.0	14
3	N3-methyl	776	1.58	13.9	90
4	N3	761	1.26	6.8	56

*catalytic conditions: 50 mg of catalyst, 10 mmol of epichlorohydrin, 10 bar of initial CO_2, 120 °C, 1 h

Acknowledgments

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Direct air capture and conversion of carbon dioxide into cyclic carbonate

Marcileia Zanatta,[1*] Eduardo García-Verdugo,[2] Victor Sans[1]

[1] *Institute of Advanced Materials (INAM), Univesitat Jaume I, Avda Sos Baynat s/n, 12071, Castellón, Spain*
[2] *Departamento de Química Inorgánica y Orgánica, Universidad Jaume I, E-12071 Castellón, Spain*
**zanatta@uji.es*

Keywords: atmospheric air • CO_2 conversion • ionic liquids

Abstract

Direct air capture (DAC) is a very attractive strategy to reduce CO_2 concentration in the atmosphere. However, the existing capturing processes are technologically challenging due to the costs of the processes and the low concentration of CO_2 to be employed as feedstock. Thus, chemisorbent materials (e.g. amines or hydroxides) have proven to be much more effective for DAC processes. This renders thermodynamically stable adducts (e.g. carbamates and carbonates), which require large amounts of energy to recover the CO_2 or low added value products (e.g. $CaCO_3$). The efficient valorisation of the CO_2 captured from extremely diluted sources could help overcome many techno-economic limitations.[1]

In previous work we demonstrated that ILs with basic and hygroscopic anions (e.g. acetate, imidazolate, hydroxide), can capture CO_2 from concentrated sources, forming HCO_3^-.[2]

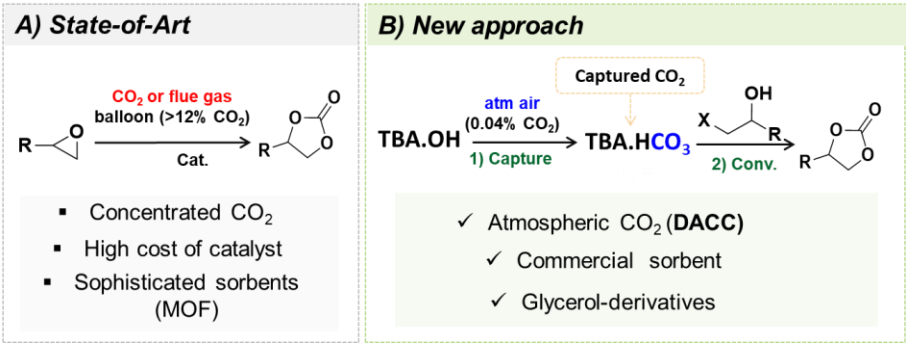

Figure 1. General approach of this work.

Here we present a novel methodology for direct air capture and conversion (DACC), able to efficiently convert CO_2 from the air into cyclic carbonates (Figure 1) . The new approach employs commercially available basic organic salts, works under mild reaction conditions without the need for sophisticated and expensive co-catalysts or sorbents. Two hypothesis have been demonstrated: (i) a solution of organic hydroxide salts can be able to capture de CO_2 directly from the air forming HCO_3^-; and (ii) the captured CO_2 (HCO_3^-) can be employed as a source of CO_2 to achieve a sequential transformation, reducing the energetic cost compared to a carbamate. Besides, the use of halohydrines derived from glycerol is advantageous from a sustainable chemistry perspective, since it derives from biomass processing waste and it avoids the use of less safe epoxides. The reaction mechanism was evaluated and the CO_2 sorbent demonstrated activity even after 3 cycles.

Acknowledgments

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Modified Red-Mud based Hydrid Catalyst for CO_2 Hydrogenation to Paraffines, Olefins and Aromatics

Aniz C Ummer, [1*] Galal Atef Nasser [2], Syed Ahmed Ali [3]

[1] *Interdisciplinary Research Center for Refining Advanced Chemicals, Research Institute, King Fahad University of Petroleum & Minerals, Dhahran 31261, KSA*

[2] *Interdisciplinary Research Center for Hydrogen and Energy Storage, Research Institute, King Fahd University of Petroleum & Minerals, Dhahran 31261, KSA*

[*] *aniz.ummer@kfupm.edu.sa*

Keywords: Red Mud, CO_2 conversion, Hydrocarbons, Metal catalyst, Fixed bed reaction

Introduction

Greenhouse gas such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and fluorinated gases are being emitted to the atmosphere and it become a major concern for industries across the globe. Conversion of CO_2 to useful chemicals can reduces their release to atmosphere and simulatanesouly result in economic benefits as well. The process of hydrogenation of CO_2 to hydrocarbons, syngas, oxygenates and aromatics has got huge response from the scientific community as these molecules are important raw materials for plastics and polymers, fine chemicals and petrochemicals. Larget number of studies are reported on developing and effective utilization of different materials as catalysts, viz. CO_2 valorization [1], ketonization [2], adsorption [3]. CO_2 hydrogenation [4] is also reported to an effective process to convert CO_2 into hydrocarbons.

Experimental/methodology.

In this work, metal oxide based by product material, namely red mud and its modified versions are utilized as catalysts (containing Fe & Al oxides in major). These mixed metal oxides mixed with zeolites to get hybrid dual function catalysts. They were characterized using X-ray diffraction (XRD), temperature program reduction using H_2 (H_2-TPR) and N_2 adsorption/desorption method etc. The catalyst samples are named as RM-1, RM-2 and RM-3. All the prepared samples were tested and their performance for CO_2 hydrogenation application was demonstrated using a fixed bed test reactor at 350°C and 40 bar pressure in down-flow mode using the feed containing CO_2 and H_2 at 1:3 ratio. The basicity and acidity of the catalysts are analyzed using temperature program desorption using carbon dioxide (CO_2-TPD) and ammonia (NH_3-TPD), respectively. Attempts have been done to understand the chemistry and mechanism of the reaction after carefully interpreting the characterization results

Results and discussion

The characterization results of the prepared samples results are showed in Table 1. RM-1 catalyst showed 11.98% CO_2 conversion whereas RM-2 and RM-3 showed 14.20 and 13.85% CO_2 conversion, respectively as shown in Table 2 and Figure 1. CO is a significant product in RM-1, whereas methane is produced in equal amounts over RM-2 and RM-3.

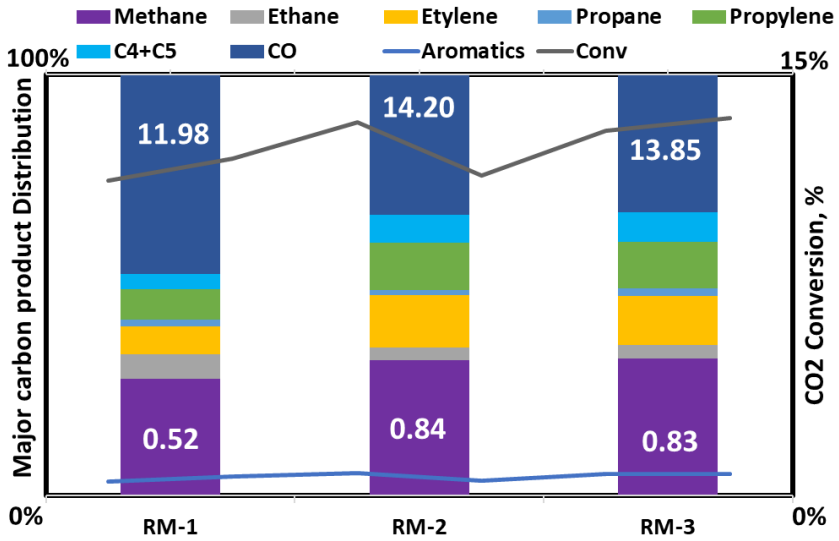

Figure 1. Catalytic performance results of some of the prepared samples for CO_2 hydrogenation

Upon modifying with the promoter, RM-3 samples showed significant improvement in olefin formation which is also reflected in its affinity towards NH_3 and CO_2. Acidity values reduced and Basicity value increased, which may enhance the CO_2 adsorption and further its reaction with H_2 to produce desired products. The difference in surface and basicity of different samples, as given in Table 1 are discussed and correlated to the performace. The presence of zeolites contribute the dehydration of the intermediate products to produce more olefins.

Table 1. Characterization results of some of the prepare samples

Sample	**RM-1**	**RM-2**	**RM-3**
BET Surface Area (m^2/g)	15.9	31.5	57
Pore volume (cm^3/g)	0.034	0.043	0.068
H_2-TPR (mmol/g)	2.71	3.87	1.35
NH_3-TPD (mmol/g)	0.003	0.004	0.014
CO_2-TPD (mmol/g)	0.036	0.07	0.295

In the similar way, aromatics formation is also enhanced over RM-2 and RM-3 as compared. Even though the aromatics production is marginal in quantity, being a high value commodity produced over a cheap catalyst using CO_2, one of the environmentally harmful gas which need immediate solutions to utilize effectively. The study includes modification and synthesis of hybrid catalysts using red mud and zeolites, characterization and catalytic evaluation of selected hybrid duab function catalysts for the hydrogenation of CO_2 to valuable hydrocarbons and chemicals

Table 2. Catalytic performance data of some of the prepared samples

Sample Name/Product(wt%)	**C1**	**C2**	**C2=**	**C3**	**C3=**	**$C4^+$**	**Arom**	**CO**	**Conv**
RM-1	27.51	5.77	6.71	1.61	7.17	3.6	0.54	47.09	11.98
RM-1	31.88	2.92	12.31	1.32	11.18	0.09	0.83	33.02	14.20
RM-1	32.28	3.19	11.62	1.62	10.95	0.11	0.82	32.49	13.85

The cheap catalytic material utilized in this study offer significant value in terms of carbon footprint achievements and utilization of industrial waste as well. The interpretation and understanding of the results will be presented.

Acknowledgments

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Hydrogenation of carbon dioxide to olefins over Co modified Fe-H-ZSM-5 catalyst

M. Cele[1*], P. Maseko, M. Mdleleni[2]
[1]*North–West University, Mafikeng Campus, Mmabutho, South Africa*
[2] *PetroSA Synthetic Fuels Innovation Centre (PSFIC), South Africa Institute of Advanced Material Chemistry (SAIAMC), University of Western Cape,* Bellville, South Africa
*mnmduduzi@gmail.com

Introduction

Using CO_2 as a raw material to generate light olefins can not only mitigate global warming, but also provide an alternative option to replace depleting fossil fuels [1]. Fe based catalysts have been extensively studied in CO_2 hydrogenation, which typically demonstrate unsatisfactory selectivity towards lower olefins [2].

Experimental

The ionic exchange method was used to produce Fe-ZSM-5 with Co and the CO_2 hydrogenation was conducted on continuous flow reactor.

Results and discussion

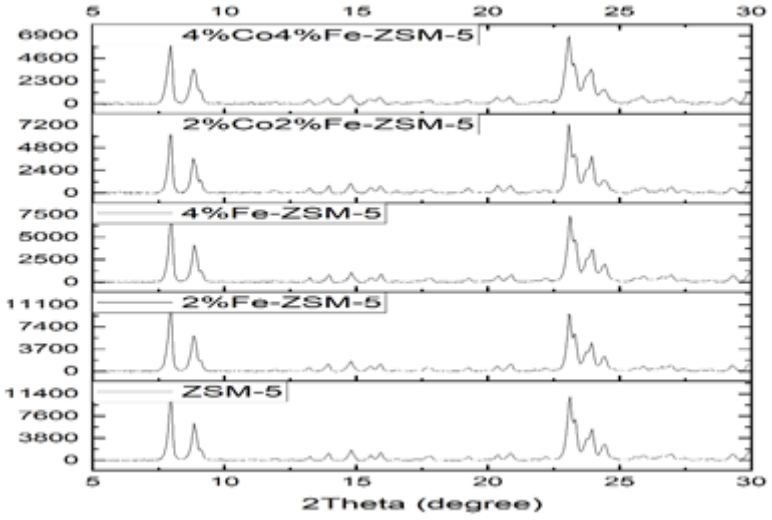

Figure 1: XRD patterns of ZSM-5 and metal modified catalysts.

Conclusion

The synthesized Fe-based catalysts were active in the CO_2 hydrogenation into hydrocarbons.

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Ni-based oxides for dry reforming of methane: Investigation of Catalytic Activity and Regeneration Capacity

Luca Consentino[1,2,*], Valeria La Parola[1], Giuseppe Pantaleo[1], Eleonora La Greca[1], Michelangelo Gruttadauria[2] and Leonarda F. Liotta[1]

[1] *Institute for the Study of Nanostructured Materials, National Research Council (ISMN-CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy*

[2] *Department of Biological, Chemical and Pharmaceutical Sciences and Technologies (STEBICEF) and INSTM UdR– Palermo, University of Palermo, Viale delle Scienze, Ed. 17, 90128 Palermo, Italy*

[*] *luca.consentino@ismn.cnr.it*

Keywords: Dry reforming, Ni-based catalyst, syngas and catalyst regeneration

Introduction.

Methane dry reforming (DRM) is an innovative process that uses heat and a catalyst to convert methane and carbon dioxide into useful products like syngas (a mixture of H_2 and CO). This process can help reduce greenhouse gas emissions and create environmentally sustainable fuels [1]. However, the DRM reaction is accompanied by several side reactions, such as methane decomposition, the Boudouard reaction and CO reduction, which can lead to deactivation of the catalyst due to the accumulation of carbon deposits [2]. For this reason and for the economic viability of the reforming processes, the regeneration of catalysts has attracted great attention. Therefore, it is crucial to design catalysts and related supports that do not undergo deactivation by coke and that can be regenerated after poisoning [3][4]. Nickel-based catalysts are often used in DRM due to their low cost, high availability, and good catalytic performance. However, they can be affected by sintering and coke deposition at high temperatures [5]. To increase the effectiveness of these catalysts, the use of different preparation conditions of the support material can affect and improve the characteristics, phase composition and distribution of the nickel phases. The aim of this study is to evaluate how the support preparation conditions influence the catalytic performance of Ni-La_2O_3 catalysts in DRM reaction. Additionally, the catalysts stability and regeneration from coke poisoning was investigated.

Experimental/methodology.

Ni-La_2O_3 catalysts were synthesized by one pot hydrothermal method (HT) and precipitation assisted by microwave irradiation (MW). The so prepared samples were compared to Ni/La_2O_3 where Ni was deposited by wetness impregnation over La_2O_3 oxides obtained by HT and MW methods. DRM reaction was carried out in a fixed-bed reactor by feeding a gas mixture of CH_4 and CO_2 (ratio 1:1) diluted in He. The physiochemical properties, redox stability and regeneration capacity of the catalysts, before and after reaction, were characterized by XRD, N_2-physisorption, H_2–TPR, O_2-TPO, TGA and XPS.

Results and discussion.

The comparison between Ni-La_2O_3 catalysts synthesized using different methods showed that the support and Ni phases composition played a crucial role in determining the nature of active sites and their dispersion. As a result, the DRM activity, redox stability and ability to regenerate from coke poisoning were strongly influenced by the catalyst preparation methods.

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Thermochemical catalysis for carbon dioxide splitting

S. Costa[1*], A. Glisenti[1]

[1]*Università degli studi di Padova, Padova, Italia*
[*]*simone.costa.2@studenti.unipd.it*

Keywords: carbon dioxide, splitting, iron spinel, thermochemical cycle.

Introduction. To prevent climate change from becoming irreversible big efforts are carried out to decrease the concentration and the emission of CO_2. A thermochemical cycle for the splitting of CO_2 can be a very good way to exploit this gas, because the catalyst, after a pre-reduction step at 1400°C and in an inert atmosphere can take the oxygen of carbon dioxide and water reducing these gases in CO and H_2[1,2,3], that is the composition of the syngas, useful for producing synthetic fuels by Fischer-Tropsch reaction. After this oxidation, the catalyst is regenerated and it can afford another cycle. The best materials for this thermochemical cycle result to be ceria[1] (CeO_2) and iron spinel[2] (Fe_3O_4) and studies on these two oxides focus on the attempt to increase stability by means of doping them and/or by supporting them with refractory materials, like ZrO_2[3]. In particular, $Ni_{0.9}Mg_{0.1}Fe_2O_4$ seems to be the catalyst that gives the best performances and stability[2]. A possibility is to investigate the use of support that can act as "co-catalysts" to allow the reduction at lower temperature with respect to Fe_3O_4. The best materials turn out to be nickel oxide and cupric oxide.

Experimental/methodology. The $Ni_{0.9}Mg_{0.1}Fe_2O_4$ iron spinel is synthetized using the citrate method[4], mixed with CuO, NiO or ZrO_2 (at 20% and 50% in weight) by wet ball milling method, then all of these compounds are characterized using XRD, SEM, EDX and XPS. To study the maximum oxygen released and successively reabsorbed by all of the materials, H_2-TPR (5% of hydrogen in helium) and O_2-TPO (5% of oxygen in helium) up to 900°C both are carried out. Also, CH_4-TPR and CO_2-TPO are carried out in order to study the reduction temperatures of materials, up to 900°C and with a concentration of active gases of 10%. The catalytic tests are performed in a dynamic bed reactor, flowing 100 sccm of 5% H_2, raising the temperature from room to 580 °C with a ramp rate of 10°C/min, flowing helium to 1000°C with the same ramp, and then 100 sccm of 10% CO_2 for 30 min at 1000°C (the gas complement is helium). Other catalytic tests are carried out, at 1000°C, flowing 100 sccm of 10% CH_4 for 30 min and then 10% CO_2 (also in this case the complement is helium). During these catalytic tests, IR and mass spectrometry are used to quantitate and observe the gases flowed and produced in the reactor.

Results and discussion. By H_2-TPR and O_2-TPO it is observed that all of the compounds released almost all of the oxygen, then reabsorb the same quantity; a different behaviour is observed for the samples mixed with zirconium oxide because this type of support is a refractory and inert material. CH_4-TPR show that NiO greatly favours the reduction of the material in methane, in fact the reduction temperature is lowered. All of the CO_2-TPO occurs immediately, at 600°C, demonstrating that the reduced phase of the iron spinel is very active for the splitting of carbon dioxide also at a low temperature, and that the reduction step of the thermochemical cycle is the one at highest temperature. Mass spectrometry showed that all of the compounds produce syngas after the reduction in methane and CO during the splitting of CO_2, and it is noticed that $Ni_{0.9}Mg_{0.1}Fe_2O_4$ mixed with NiO at 20% in weight is the material with best performances and stability, both using H_2 or CH_4 as reductant atmosphere. After two thermochemical steps, SEM images showed the very high sintering of samples with copper oxide due to his low melting temperature and no sintering on the sample supported by ZrO_2.

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CO_2 valorization on metal based mesoporous silica

M. Dan[1], O. Grad[1], A. Kazsa[1], M. Mihet[1], M.D. Lazar[1]

[1]*National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania*
monica.dan@itim-cj.ro

Keywords: silica mesoporous materials, Ni catalysts, CO_2 methanation

Introduction.

In the actual context of global warming the economic and the scientific community are compelled to search for better strategies for sustainable resources. The transformation of greenhouse gas CO_2 into valuable chemicals might prove one solution to this problem. A known and potential feasible technology is the CO_2 methanation consisting in hydrogen reduction of CO_2, thus transforming the CO_2 into synthetic methane. Although this technology has been investigated on large variety of metal catalyst like Ni, Ru, Rh [1] improvements can be done in order to enhance catalytic activity and stability of the catalytic material. Thus, highly accessible silica supports (SBA-15, FDU-12) with high surface areas and stability might improve the dispersion of the active metal nanoparticles species, which may lead to a better catalytic performance.

Experimental/methodology.

Catalyst synthesis

The support of the catalyst has been prepared following Zhao [2] method and the Ni metal nanoparticles were deposited on the support via different techniques : **wet impregnation (IMP)** which consists in adding the nickel nitrate hexahydrate precursor dissolved in water to the mesoporous silica support, followed by a heat treatment step and **melting infiltration (MI)** a method based on grinding together the mesoporous support and the nickel nitrate hexahydrate, subsequently subjected to a heat treatment step.

Catalyst Characterization

From the N_2 adsorption−desorption isotherms it was determined the specific surface area and pore structure of the catalysts. The crystalline phases and the dimension of Ni crystallites were determined through X-ray diffraction. Transmission electron microscopy measurements and thermogravimetry analyses completed the structural characterization. The used catalysts were also subjected to all these characterizations.

Evaluation of Catalyst activity

The performance of catalysts was assessed in a fix bed reactor under atmospheric pressure. The catalyst was reduced in hydrogen prior to testing. The evaluation of the catalyst was performed at different temperatures (100-500°C). The outcome composition of the effluent gas was analyzed by gas chromatography.

Results and discussion.

From the characterization methods we can conclude that the prepared catalytic materials present a uniform dispersion of the metallic Ni nanoparticles. For catalysts prepared by MI the NiNPs were found mainly inside the pores of the mesoporous silica support. Regarding the catalytic activity it has been observed that even at low temperature the catalytic material is able to convert the CO_2. The major components obtained in the reaction are CH_4 and H_2O, but also small amounts of CO were detected. The catalysts prepared by MI method are more active and stable than those prepared by IMP, in accordance to their better structural properties and higher capacity to adsorb and activate hydrogen. As a conclusion, the attained results might present a significant contribution in developing highly active and stable catalysts for CO_2 methanation.

Acknowledgments

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Effects of zeolite acidity on catalytic performance and coking behavior for CO_2 to light olefins using bifunctional composite catalysts

Wei Di[1], Abdenour Achour[1], Phuoc Hoang Ho[1], Oleg Pajalic[2], Lars Josefsson[3], Louise Olsson[1] and Derek Creaser[1 *]

[1] *Chemical Engineering, Competence Centre for Catalysis, Chalmers University of Technology, Chalmers University of Technology, Gothenburg, Sweden*
[2] *Perstorp AB, Perstorp, Sweden*
[3] *Josefsson Sustainable Chemistry AB, Stenungsund, Sweden*
[*] *derek.creaser@chalmers.se*

Keywords: CO_2 hydrogenation, light olefins, bifunctional catalysts, SSZ-13 zeolite, acidity

Introduction. Effectively converting waste CO_2 into basic chemical feedstocks opens up a sustainable way to produce green chemicals in the future. Over an oxide-zeolite catalyst with the bifunctional active sites for CO_2 hydrogenation and C−C bond formation, CO_2 can be converted via the intermediate methanol into a mixture of short-chain olefins [1]. Previously, few investigations have been devoted to studying the low-temperature performance of bifunctional catalysts in CO_2 hydrogenation since the quick deactivation caused by coking. Inspired by the fact that the hydrogenation catalyzed by Brønsted acid sites (BAS) can inhibit coke deposition during the MTO reaction [2-3], here the effect of zeolite acidity on both olefin distribution and coke deposition is explored during low-temperature CO_2 hydrogenation with the aim to boost the selectivity for light olefins. This is done with In_2O_3/SSZ-13 bifunctional catalysts synthesized with varying BAS density.

Experimental/Methodology. The Na-SSZ-13 zeolite with varied Brønsted acid sites was post-synthesized by exchanging the proton-type of SSZ-13 (Si/Al=15) zeolite with a sodium nitrate solution, the obtained Na-SSZ-13 zeolites were mixed with In_2O_3 oxides to get the bifunctional catalysts. The fresh catalysts and individual ingredients were characterized by XRF, XRD, BET, NH_3-TPD, and SEM, and the spent catalysts were analyzed by using TPO, TG, and GC-MS. The CO_2 hydrogenation experiments were performed in a flow reactor with 1g total of bifunctional catalysts under 1 MPa, 325℃, 6400 h^{-1} of GHSV with H_2: CO_2 molar feed ratios at 6:1. Products were analyzed by online GC.

Results and discussion. Exchanging from proton to sodium ions can significantly reduce the BAS density of the SSZ-13 zeolite and the BAS density of SSZ-13 zeolite influences the performance of the bifunctional catalyst during the CO_2 hydrogenation process. At the beginning of the reaction, it affects the initial transient behavior. Specifically, the catalyst with low BAS density shows a low methanol conversion rate, where unreacted methanol appears in the effluent at the beginning. Methanol gradually decreases to zero when the organic co-catalytic centers (Hydrocarbon pool species, HPC) are established. At the same time, the accumulation of methanol also causes a higher CO selectivity during the initial stage. With higher conversion of methanol, the selectivity to CO also decreases to its steady-state value as the reaction proceeds. The BAS density of the catalyst also strongly impacts the hydrogenation of olefins, and the formation of aromatics and coke precursors. The lower the BAS density of the catalyst, the slower rate of hydrogenation, which gives higher selectivity for light olefins in the product. However, the weakened hydrogenation will also promote the proliferation of coking precursors. The characterization of spent catalysts showed that the catalysts with low BAS density experienced a rapid coke deposition rate. In particular, compared with polycyclic aromatics, adamantanes are abundant on the deactivated catalysts. Their formation was strongly correlated with emissions of unreacted methanol during the initial stage of reaction, which may be one of the most important reasons for catalyst deactivation. It is necessary to avoid harmful coke formation while adjusting BAS to increase the yield of olefins.

Acknowledgments
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Advancement of design of Ni/$Ce_{0.8}Ti_{0.2}O_{2-\delta}$ for the dry reforming of methane using transient and isotopic techniques

C.M. Damaskinos, M.A. Vasiliades and A.M. Efstathiou*

Department of Chemistry, Heterogeneous Catalysis Laboratory, University of Cyprus, Nicosia, CY
**A.M. Efstathiou: efstath@ucy.ac.cy*

Keywords: dry reforming of methane, syngas, doped ceria, supported Ni catalysts, coking.

Introduction

The discovery of several Natural Gas reservoirs rich in CO_2, and the progress in biogas production and CO_2 capture emissions, has attracted resurgent interest in the dry reforming of methane reaction (DRM: $CH_4+CO_2 \leftrightarrow 2CO+2H_2$). Supported Ni catalysts are mainly explored but they suffer from severe carbon deposition and deactivation. To face this problem, there is a need of knowing the fundamental kinetics of carbon deposition (via CH_4 decomposition and Boudouard reaction) and removal steps (via support's lattice oxygen, O_L) in the DRM (**Fig. 1A**), and this was the aim of the present work [1].

Experimental/methodology

x wt% Ni/$Ce_{0.8}Ti_{0.2}O_{2-\delta}$ (x = 3-10) were synthesized aiming to investigate the effect of Ni particle size (ca. d_{Ni} = 22-45 nm) on important kinetic and mechanistic parameters of carbon paths in the DRM reaction. The influence of d_{Ni} (nm) on the surface coverage (θ), mean residence time (τ), rate constant of RDS (k_{eff}) of *active* carbon-containing species, and oxidation of carbon by the support's lattice oxygen were investigated by SSITKA (use of $^{13}CO_2$ and $^{13}CH_4$) and other protocols of using transient $^{18}O_2$ isotopic experiments.

Results and discussion

The amount (N_C, μmol g^{-1}) and mean residence time (τ, s) of *active* C-containing intermediates formed in the *CO_2 activation route* (SSITKA switch: $^{12}CO_2/^{13}CO_2$) were found to increase with increasing TOS (0.5 to 16 h) and d_{Ni} (22-45 nm). Similarly, the concentration (N_{CO2}) of *inactive* reversibly adsorbed CO_2 (carbonate-type species) that potentially influence the mobility and concentration of *active* O_L species, likely affecting the oxidation rate of C, were found to increase. An *active* -CH_x of $\theta_C \sim 1$ was formed via dissociation of CH_4 on Ni, and this was probed for the first time by SSITKA ($^{12}CH_4/^{13}CH_4$ switch). A small amount of active O_s and/or O_L participates in the formation of CO_2 via oxidation of C derived from CH_4. The θ_C and τ_C were found to increase with increasing d_{Ni} and TOS. Also, τ_C was an order of magnitude larger than that related to the CO_2 activation route. This implies that the RDS in the C-path of CH_4 activation is slower compared to that in the CO_2 activation path. The small Ni particles (d_{Ni} = 22 nm) was found to accumulate lower amounts of carbon (~ 300 times) compared with the larger ones (32-45 nm) after 100 h DRM (20%CH_4, CH_4/CO_2=1; 750 °C). **Fig. 1B** depicts the dynamic rate evolution of $C^{18}O(g)$ and $C^{16}O(g)$ formation (normalized to the number of Ni particles/g_{cat}) obtained during DRM following $^{16}O/^{18}O$ exchange at 750°C [1]. The $C^{18}O(g)$ is due to the oxidation of C (derived from CH_4) by lattice $^{18}O_L$, while $C^{16}O(g)$ is due to the oxidation of C by ^{16}O-s (s: Ni) derived from CO_2 [1]. The R($C^{18}O$) at the initial stage of the transient was described by: R($C^{18}O$) = k_{app} $C_{O\text{-}L}$ C_C ($C_{O\text{-}L}$ is the concentration of lattice ^{18}O, and C_C that of carbon nearby the Ni-support interface). The small Ni particles present the lowest R($C^{18}O$) (**Fig. 1C**) but possess the largest k_{app} compared to those for d_{Ni} = 32-45 nm. Thus, small Ni particles become more active towards carbon oxidation by O_L, and this agrees with the lowest amount of carbon accumulated per gram of catalyst for the small Ni particles.

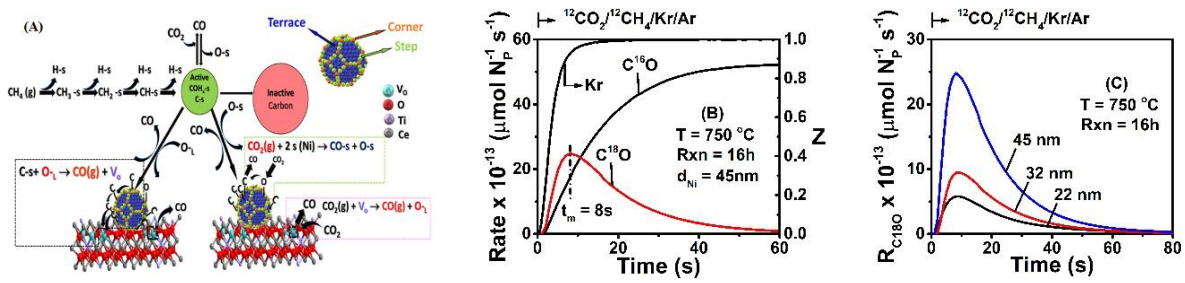

Figure 1: (A) Reaction network of catalytic DRM on Ni/$Ce_{0.8}Ti_{0.2}O_{2-\delta}$; (B)-(C) Transient rates of $C^{16}O$ and $C^{18}O$ formation obtained during DRM following $^{16}O/^{18}O$ exchange at 750 °C, as a function of d_{Ni} (nm).

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Experimental and theoretical approach on understanding the Ni-supported Pr-doped CeO_2/Al_2O_3 catalysts for CO_2 methanation

A. Alkhoori[1], A. Dabbawala[1], M. Harfouche[2], O. Elmutasim[1], M. Vasiliades[3], N. Charisiou[4], D. Anjum[1], M. Baker[5], M. Goula[4], A. Efstathiou[3], K. Polychronopoulou[1*]

[1]*Khalifa University, Center for Catalysis and Separation (CeCaS), Abu Dhabi, United Arab Emirates P.O. Box 127788, Abu Dhabi, United Arab Emirates*
[2]*Synchrotron-Light for Experimental Science and Applications in the Middle East (SESAME), 19252, Jordan*
[3]*Department of Chemistry, Heterogeneous Catalysis Laboratory, University of Cyprus, 2109, Nicosia, Cyprus*
[4]*Laboratory of Alternative Fuels and Environmental Catalysis (LAFEC), Department of Chemical Engineering, University of Western Macedonia, 50100, Kozani, Greece*
[5]*University of Surrey, Guildford, GU2 4DL, United Kingdom*
[*]*kyriaki.polychrono@ku.ac.ae*

Keywords: Power-to-gas, CO_2 Methanation, Ni-supported catalyst, Pr-doped CeO_2.

Introduction. The increasing CO_2 concentration in the atmosphere is one of the major concerns of the 21st century due to the adverse environmental effects associated with it [1]. This has led to intensive research efforts in CO_2 mitigation technologies. Recently, power-to-gas technologies have been gaining ground proving their reliability in providing green H_2 for CO_2 reduction to value-added chemicals such as CH_4, C_2H_4, or CH_3OH. In this study, efficient Ni catalysts supported on Pr-doped ceria are designed and the interfaces involved are investigated for CO_2 methanation reaction.

Experimental/methodology. Pr-doped ceria (CP) modifier and Ni metal (10 wt.%) are both incorporated into porous alumina with different textural properties (i.e., low-porosity (LA), and high-porosity (HA)). The physicochemical properties of both calcined and reduced catalysts are investigated via different techniques. The catalytic activity/stability tests are obtained in a fixed-bed tubular microreactor from 200-500°C. Kinetics studies and DFT computations are carried out to obtain activation energies and configuration geometries for the CO_2/H_2 co-adsorption, respectively. Catalysts are coded as NCP-HA, NCP-LA, and NCP (bare, no alumina).

Results and discussion. The highest conversion is obtained at 350°C reaching a value of 75% for the best performing catalyst with an accompanied selectivity to CH_4 of >98%. Different spectroscopy and microscopy tools are used to unveil the intrinsic characteristics of the catalysts due to the perplex structure of the latter. Ni K-edge Synchrotron EXAFS demonstrates difference in local structure among the NCP-HA, NCP and NCP-LA catalysts. Ce L_3 edge analysis shows that the presence of Al_2O_3 as dispersion medium impacts the Pr oxidation state (more metallic Pr in the absence of Al_2O_3). Additionally, Ni dispersion (H_2-TPD) is found in the 18-37% range with a strong effect of Al_2O_3 textural features; good agreement with the HRTEM Ni^0 particle size (7-15 nm) is found. RGB (STEM-HAADF) shows the well dispersion of all elements on the high-porosity Al_2O_3 support. Structural studies, as implemented through Raman spectroscopy, along with the Ce 3d XPS spectra confirms oxygen vacancy presence and deficiency, in the bulk and surface, respectively. The apparent activation energy (E_a) of the CO_2 methanation over the here in investigated catalysts is around 53.7-68.8 kJ/mol; these values are much lower than that reported in the open literature for similar composition catalytic systems, such as Ni/Al_2O_3 (E_a = 80 kJ/mol) [3], and Ni/Pr10Ce (93 kJ/mol) [4]. For the DFT calculations, Ni_{13}/Pr-CeO_2 surface is used; the DFT calculations prove the bifunctional character of the catalyst, where H_2 adsorbs/dissociates on Ni^0, and CO_2 is simultaneously bonded to both Pr^{4+} and Ce^{3+} atoms (bridged site) as the most favorable site with the strongest binding energy of -1.25 eV.

Acknowledgments

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Incorporation of an alkaline-alkaline earth metal in an unsupported bimetallic Ni-containing catalyst for the CO_2–SR technology

S. Essounani*, S. Molina-Ramírez, M. Cortés-Reyes, C. Herrera, M.A. Larrubia, L.J. Alemany*

Departamento de Ingeniería Química, Facultad de Ciencias, Universidad de Málaga 29071, Málaga, Spain
**sofiaess@uma.es, luijo@uma.es*

Keywords: CO_2-capture, CO_2-SR technology, greenhouse gasses valorization, hybrid catalysts.

Introduction.

In the past decades, global warming resulting from the emission of greenhouse gases, consisting mainly of carbon dioxide and methane, has become one of society's main concerns. In this context, there has been a growing interest in developing technologies that allow the capture and storage of CO_2 in an economical and sustainable way. The application of a heterogeneous bimetallic nickel-barium catalyst as a dual material has been studied for its use in the CO_2 regeneration cyclic process [1]. The present work shows the data corresponding to the substitution of Ba by Ca or Sr and K as a bimetallic catalytic systems to analyse the structural and physicochemical properties and the effect on CO_2 storage capacity.

Experimental/methodology.

The catalysts were synthesised by an ultrasonic assisted coprecipitation of the heterometallic mixed precursors employing an atomic ratio Ni:Me = 1:1 using colloidal silica as surface area promoting agent, and calcined at 800 °C in air for 4 h.

X-ray diffraction (XRD), KBr-FTIR infrared, Raman spectroscopy and nitrogen adsorption-desorption were employed for the characterisation. The CO_2 adsorption capacity was analysed at low temperature and at high reaction temperature.

Results and discussion.

The influence of the incorporation of the metal in combination with nickel has been studied and it has been found that, even at high temperature, it maintains a cubic structure with a surface area higher than 80 $m^2 \cdot g^{-1}$. The crystal size of bivalent or monovalent cation was not affected by the modification of the catalytic formulation. There is a correlation between CO_2 adsorption capacitity and the electronegativity of the second metal incorporated to the nickel structure as shown in Figure 1.

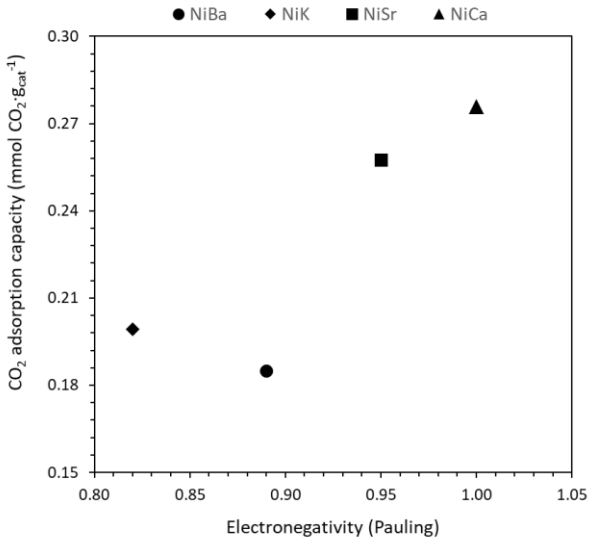

Figure 1. CO_2 adsorption capacity of the catalysts at 25°C versus the electronegativity of the metal incorporated.

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Dynamic Interaction of CO_2 with a Ru/γ-Al_2O_3 Catalyst – A Temporal Analysis of Products (TAP) Study

Corinna Fauth[1*], Anja Lenzer[1], Ali M. Abdel-Mageed[1,2], R. Jürgen Behm[1,3]

[1]*Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany*
[2]*Leibniz Institute for Catalysis (LIKAT Rostock), D-18059 Rostock, Germany*
[3]*Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany*
[*]*corinna.fauth@uni-ulm.de*

Keywords: CO_2 reduction, active oxygen deposition, Ru/Al_2O_3 catalyst, temporal analysis of products (TAP)

Introduction. Ruthenium nanoparticles (NPs) supported on inorganic oxides act as highly active catalysts for several reactions, including the methanation of CO or CO_2 [1], the oxidation of CO [2], the Fischer-Tropsch reaction [3], or the reverse water-gas shift (RWGS) reaction [4]. In all these reactions, the interaction of CO_2 with the catalyst plays an important role. Thereby the reaction may occur in an associative or dissociative way, which possibly involves changes in the oxidation state of Ru. Aiming at a detailed picture of the interaction of CO_2 with Ru or supported Ru catalysts we investigated the dynamic reduction and oxidation of Ru/Al_2O_3, exploring the reversible replenishment of active oxygen by interaction with CO_2 by temporal analysis of products (TAP) reactor measurements under well-defined reaction conditions. In these multi-pulse experiments, we compared the oxidation strength of O_2 and CO_2 pulses and further investigated the interaction of isotope marked $C^{18}O_2$ with the catalyst and adsorbed species present on the catalyst.

Experimental/methodology. We used a commercial 5.0 wt.% Ru/γ-Al_2O_3 catalyst (100 m^2 g_{cat}^{-1}, mean Ru particle diameter 1.6 nm) supplied by Johnson Matthew. After pretreatment in 10% O_2/N_2 at 150 °C for 30 min (O150) the catalyst was exposed to pulse sequences. We performed the multi-pulse experiments in a home-built TAP reactor described in ref. [5]. Piezo-electrically driven pulse valves generated gas pulses (1.5-3.2×10^{16} molecules per pulse) with high reproducibility. The effluent gas from the catalyst bed, which was fixed in a quartz glass microreactor, was detected by a quadrupole mass spectrometer (QMG 700, Pfeiffer) located in a UHV chamber (background pressure 8×10^{-9} mbar).

Results and discussion. First, the reversible removal and replenishment of active oxygen on Ru/Al_2O_3 was monitored during alternating sequences of CO/Ar and O_2/Ar pulses at 190 °C, 250 °C, and 300 °C. The amount of active oxygen removal was determined from the amount of CO consumed or CO_2 formed in the CO pulse titration. At all temperatures, the CO pulses were able to completely reduce the RuO_2 particles formed during the O150 pretreatment, resulting in CO_2 pulses that left the catalyst bed, but also carbonate species which remained adsorbed on the support. In the following sequence of O_2 pulses approx. 60% of the initial oxygen content could be replenished at 190 °C, and this fraction increased with higher reaction temperature. Similar experiments using CO_2 instead of O_2 pulses demonstrated that also CO_2 is able to deposit oxygen on the pre-reduced Ru surface, but the deposition rate is significantly lower compared to O_2. In the presence of H_2 the amount of active oxygen deposition by CO_2 was significantly increased to a level comparable to that of O_2, which we attribute to the formation of highly reactive water (RWGS reaction). Finally, in multi-pulse experiments with isotope marked $C^{18}O_2$ on the pre-reduced catalyst, we followed the simultaneous i) deposition of active oxygen on the surface, ii) oxygen exchange between CO_2 and adsorbed species, and iii) decomposition of surface carbonate species.

In conclusion, the interaction of CO_2 with Ru/Al_2O_3 includes both changes in the Ru oxidation state and in the adsorbate layer under reaction conditions. Therefore, these TAP measurements are highly relevant for the mechanistic understanding of various catalytic reactions on supported Ru involving the CO_2.

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Influence of the catalyst activation temperature on the ethanol production in the CO_2 hydrogenation over Cu-UiO-67

Luana do N. R. de Paula[1], Janaina F. Gomes[1], José Mansur Assaf[1*]
[1]*Federal University of São Carlos, São Carlos, Brazil*
[*]*mansur@ufscar.com.br*

Keywords: CO_2 hydrogenation, UiO-67, metal-organic frameworks, reduction temperature

Introduction. CO_2 hydrogenation to higher alcohols, linked to the use of renewable energy, is a promising approach due to possibility of reducing dependence on fossil resources [1]. Nevertheless, catalysts with adequate selectivity and activity have not yet been found. In addition, the deactivation of catalysts, especially those based on Cu, has also been a challenge to be solved. Metalorganic frameworks (MOFs), e.g. UiOs, have been studied as support for Cu catalysts and have the potential to fill such gaps, since the control of specific sites and the protection of them from agglomeration is possible, making MOFs supported catalysts more selective to ethanol and more stable under reaction conditions [1,2]. Another obstacle of this reaction is the use of H_2 from fossil resources as a co-agent, since cleaner H_2 technologies are still not viable. Water, on the other hand, can be used as an alternative hydrogen source in the hydrogenation of CO_2 to alcohols [3]. In the present work, Cu-UiO-67 was synthesized, characterized, and applied to the CO_2 hydrogenation at atmospheric pressure and using water steam as hydrogen source, aiming to study the influence of the temperature of the catalyst activation on the ethanol production.

Experimental/methodology. The methodology used to produce UiO-67 was based on An et al. [4]. Briefly, UiO-67 was synthesized by the solvothermal method for 48 h at 120°C. Copper (20 wt.%) was incorporated into the MOF structure via ion exchange. Before the reaction, the catalyst was activated under H_2 stream at temperatures between 180-240 °C for 1h. CO_2 hydrogenation to alcohols was carried out at atmospheric pressure, using water steam as hydrogen source to the reaction. Products were quantified via GC-FID.

Results and discussion. In Fig 1(a), the H_2-TPR profile shows two overlapping peaks with different intensities, centered at 237 °C and 260 °C, both associated with the direct reduction of Cu^{2+} to metallic copper [5]. The catalyst activation was performed in the range between 180 and 240 °C. After CO_2 hydrogenation at 180 °C with water steam, the samples were investigated by XRD, as shown in Fig 1(b). The formation of Cu^{+} was favored with increasing activation temperature, as evidenced by the growing intensities of the peaks at 35.6° and 42.7°, assigned to (111) and (200) diffraction planes of Cu_2O, respectively. According to Fig. 1c, the production of ethanol augmented with increasing catalyst activation temperature, reaching 5.7 $\mu mol_{EtOH}/h.g_{Cu}$ for the activation temperature of 240 °C. This performance may be associated with the formation of Cu^{+} species in the catalyst.

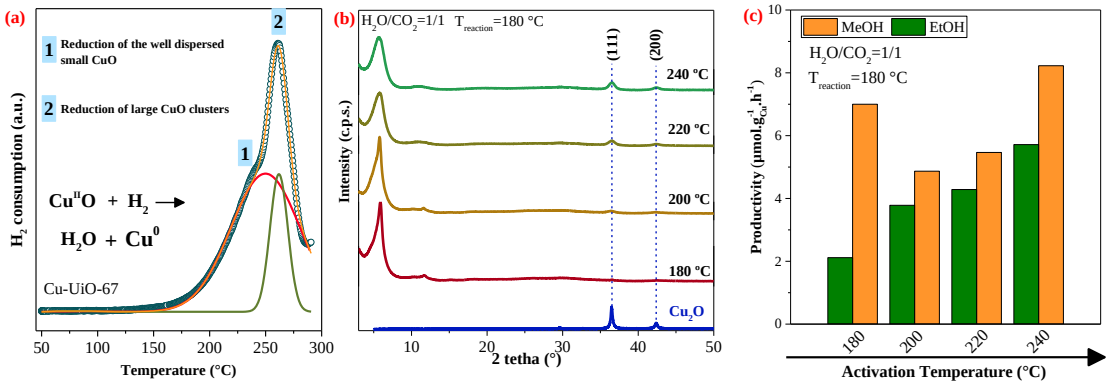

Figure 1. TPR-H_2 of Cu-UiO-67 (a); XRD of Cu-UiO-67 after CO_2 hydrogenation reaction using different activation temperatures (b); Effect of the activation temperature on the alcohols productivity (c).

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Propylene production via oxidative dehydrogenation of propane with carbon dioxide over composite metal oxides

A. Florou[1], G. Bampos[2], P. Panagiotopoulou[1*]

[1]*Technical University of Crete, Chania, Greece*
[2]*University of Patras, Patras, Greece*
[*]*ppanagiotopoulou@tuc.gr*

Introduction. Propylene (C_3H_6) is a versatile precursor for the formation of various derivatives (e.g. polypropylene, acrylic acid, acrylonitrile, cumene etc.) used in our daily life and thus, it is considered as a key component of the chemical industry [1]. Oxidative dehydrogenation of propane (C_3H_8) in the presence of CO_2 has recently gained interest as an alternative approach for the selective production of C_3H_6. This approach has the advantage that CO_2 participates both in (a) C_3H_8 conversion toward C_3H_6 and (b) hydrogen consumption via the Reverse Water-Gas Shift (RWGS) reaction [2]. Removing hydrogen from the gas stream can overcome the equilibrium limitations of C_3H_8 dehydrogenation, resulting in higher C_3H_6 yields. However, depending on the catalyst and reaction conditions employed, the reactions of C_3H_8 hydrogenolysis and C_3H_8 or C_3H_6 decomposition may also take place, resulting in a decrease of C_3H_6 yield and possibly surface carbon formation. Thus, in order for this method to be effective, the physicochemical characteristics of catalyst and operating reaction conditions should be properly selected.

Experimental/methodology. Composite metal oxide powders 10 wt.% M_xO_y-TiO_2 and 10 wt.% M_xO_y-SiO_2 (M: Ga, Cr, Ca, Sn) were prepared employing the wet impregnation method by using commercial TiO_2 or SiO_2 powder and an aqueous solution of the M_xO_y precursor salt. The impregnation was followed by drying at 120 °C for 24 h and subsequent calcination at 600 °C for 3 h. Catalysts were characterized employing nitrogen physisorption at -196°C and X-Ray Diffraction (XRD). Catalytic performance tests were carried out in the temperature range of 550-750°C using a CO_2:C_3H_8 molar ratio equal to 5:1.

Results and discussion. Results showed that the addition of metal oxides on TiO_2 or SiO_2 surface results in higher C_3H_8 conversions (X_{C3H8}) compared to bare TiO_2 or SiO_2. In the case of M_xO_y-TiO_2 catalysts, catalytic performance is improved following the order TiO_2 (none)< SnO_2 < Cr_2O_3 < Ga_2O_3 < CaO, whereas in the case of M_xO_y-SiO_2 catalysts, the activity order was found to be SiO_2 (none) < CaO < Ga_2O_3 < SnO_2 < Cr_2O_3. In all cases the main products detected were C_3H_6, CO, CH_4 και C_2H_4. Selectivity toward C_3H_6 (S_{C3H6}) was found to be higher for Ga_2O_3-TiO_2, Cr_2O_3-TiO_2, Cr_2O_3-SiO_2 and SnO_2-SiO_2 catalysts and progressively decreases with increasing temperature for all catalysts examined with the exception of the CaO containing samples, where S_{C3H6} remains stable in the entire temperature range examined. Carbon monoxide selectivity also decreases with increasing temperature above 660 °C and was found to be higher for CaO-TiO_2 and CaO-SiO_2 catalysts. Production of both CO και C_3H_6 indicates that, under the present experimental conditions, the desired reaction of oxidative dehydrogenation of propane takes place whereas part of the produced CO may be due to the RWGS reaction. Selectivities toward CH_4 και C_2H_4 exhibit similar behavior with temperature and increases slightly for T>650 °C, most possibly due to enhancement of their production via C_3H_8 hydrogenolysis and C_3H_8 or C_3H_6 decomposition reactions. Comparison of the results obtained for the two series of catalysts investigated implied that M_xO_y-SiO_2 catalysts are more active than M_xO_y-TiO_2 and exhibit significantly higher improvement compared to bare SiO_2 than that obtained for M_xO_y-TiO_2 samples. This is also the case for propylene yield which was found to be optimum for SnO_2-SiO_2 sample reaching the value of 30% at 730°C. DRIFTS studies have been also performed over selected catalysts in order to identify the nature and population of active surface intermediates and investigate the reaction pathway.

Acknowledgments

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Carbon nanobeads as active components for the production of methanol via CO_2 hydrogenation

G. Bonura, S. Todaro, C. Cannilla, A. Cajumi, J.F. Pérez Robles, F. Arena and F. Frusteri
CNR-ITAE "Nicola Giordano" Via S. Lucia Sopra Contesse 5 – 98126 Messina (Italy)
*Corresponding Author : francesco.frusteri@itae.cnr.it

Keywords: CO_2 hydrogenation, Carbon nanobeads, CuZnZr catalyst, Methanol production

Introduction.
Methanol production via CO_2 reduction in presence of renewable hydrogen represents a topic of strategic interest in view of containing the carbon footprint in atmosfere. Although several catalytic systems have been so far investigated [1,2], the obtainment of high methanol selectivity at high CO_2 conversion level (>20%) remains a problem to overcome. To achieve this target, the promotion of CO_2 activation over specific surface sites is crucial and, furthermore, it is also necessary to address the problem of the presence of water which negatively influences the activity and stability of the catalyst. In this work, the performance of Cu-ZnO-ZrO_2 (CZZ) promoted by carbon nanobeads was investigated in the synthesis of methanol by comparing results with those obtained by using a previously optimized unsupported CZZ catalyst [2].

Experimental/methodology.
The carbon nanobeads (CNBs) were functionalized to anchor a methanol phase (CZZ) through the gel oxalate coprecipitation method, according the procedure elsewhere described [2]. Catalysts were characterized by several techniques (BET, XRD, TPR, TPD, SEM, TEM, etc…) and tested in a fixed bed reactor operating at 30 bar and 260 °C by feeding a stream of $CO_2/H_2/N_2$ (23/69/8 v/v) at 8,800 $NL/kg_{Cu}/h$.

Results and discussion.
Catalytic results are shown in Fig. 1. Apart from the bare sample containing only carbon (CNBs) which shows no activity, the carbon supported sample displays a superior catalytic performance compared to the unsupported sample (CZZ), especially in terms of CO_2 conversion (21.2% *vs.* 15.6%), which leads to a higher methanol yield (8.2% *vs.* 4.6%).

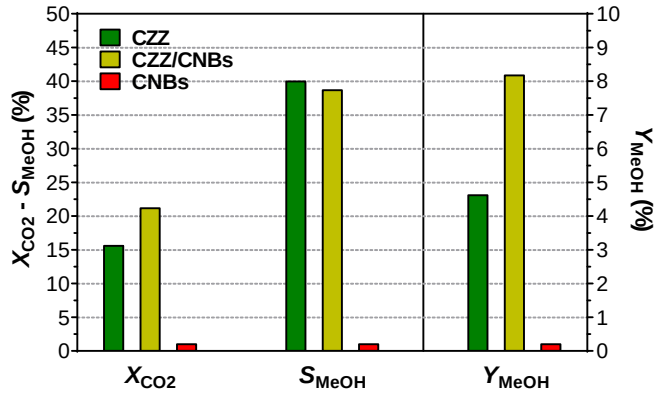

Fig. 1. Catalytic data (X_{CO2}, S_{CO}, S_{MeOH}, Y_{MeOH}) in the CO_2 hydrogenation reaction (Experimental: 260 °C; 30 bar; $CO_2/H_2/N_2$, 23/69/8 v/v; 8,800 $NL/kg_{Cu}/h$).

These results put clearly in evidence the beneficial effect obtained by the presence of carbon nanobeads in driving the production of methanol via direct CO_2 hydrogenation. This positive effect is not definitely understood, but very probably the carbon surface brings effective sticking points for CO_2 activation, also depressing the effect of water on catalyst lifetime. To demonstrate the specificity of carbon during reaction, IR measurements *in operando* conditions are in course.

Acknowledgments
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Continuous Flow Synthesis of 2-Imidazolidinone from Ethylenediamine Carbamate over the CeO_2 Catalyst

R. Fujii[1,2], M. Yabushita[2], D. Asada[3], M. Tamura[4], Y. Nakagawa[2], A. Takahashi[2], A. Nakayama[3], K. Tomishige[2*]

[1]*Organic Research Laboratory, Tosoh Corporation, Shunan, Japan*
[2]*School of Engineering, Tohoku University, Sendai, Japan*
[3]*Guraduate School of Engineering, The University of Tokyo, Tokyo, Japan*
[4]*School of Engineering, Osaka Metropolitan University, Osaka, Japan*
[*]*tomishige@tohoku.ac.jp*

Keywords: CeO_2, CO_2, 2-imidazolidinone, ethyleneurea

Introduction. 2-Imidazolidinone (EU) is a raw material for pharmaceuticals and resin additives. We reported that EU can be synthesized from ethylenediamine carbamate (EDA-CA) using CeO_2 as a heterogeneous catalyst and EDA as a solvent for EDA-CA (Fig. 1(a)) [1]. However, the generated EU sequentially reacts with EDA to form *N*,*N*'-bis(2-aminoethyl)urea (LU), resulting in low selectivity of EU (yield of EU 62% and LU 38% from EDA-CA) with a batch reactor. The formation of LU from EU and EDA proceeds easily in liquid phase without CeO_2 catalyst (Fig. 1(b)). Meanwhile, flow-type reaction has a great potential to suppress such sequential reaction since this type of reaction can be operated even at very low solvent/catalyst ratios that cannot be applied to batch reactions due to a lack of smooth stirring. Thus, in this study, we attempted to synthesize EU by applying a fixed-bed flow reactor [2].

Experimental. Granulated CeO_2 (Daiichi Kigenso Kagaku Kogyo, calcined at 873 K for 3 h in air) was used as a catalyst. An upflow-type fixed-bed tubular reactor was used with an HPLC pump. The standard reaction conditions were as follows: catalyst amount W_{Cat} 0.50 g; an EDA-CA (9.2 mol%) solution in EDA (90.8 mol%) as a reaction solution; substrate flow rate F_{Sol} 0.60 mL h^{-1} ($F_{EDA\text{-}CA}$ 0.82 mmol h^{-1}); contact time $W_{Cat}/F_{EDA\text{-}CA}$ 0.61 g h $mmol^{-1}$; and temperature 363 K. Quantitative analysis of the products and unreacted EDA-CA was performed by ^{1}H NMR and GC-FID. Selectivity and yield were calculated on an ethylene chain basis.

Results and discussion. The dependence of product selectivity on contact time ($W_{Cat}/F_{EDA\text{-}CA}$) was initially investigated at 363 K (Fig. 2). The yield of EU increased with an increase in $W_{Cat}/F_{EDA\text{-}CA}$ and reached as high as 94% at $W_{Cat}/F_{EDA\text{-}CA}$ of 3.5 g h $mmol^{-1}$. The yield of LU also increased slightly at the higher contact time but was still 1% when the maximum EU yield was provided. Therefore, the flow-type reaction greatly improved the selectivity of EU, compared to our previous batch reaction [1]. The detailed kinetic study revealed that this difference in selectivity is because the flow-type reactor enables the reaction operation even at the low W_{EDA}/W_{Cat} ratios. Under such conditions, the formation of EU from EDA-CA, whose apparent activation energy (E_a) was experimentally determined to be 97 kJ mol^{-1}, becomes faster than the latter step of LU formation from EU and EDA (E_a = 114 kJ mol^{-1}). We also found by ^{13}C CP/MAS NMR that in long-term operation, CeO_2 was gradually deactivated due to the deposition of polyurea-like compounds on the surface.

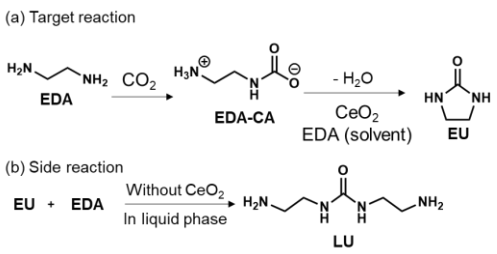

Fig. 1. Synthetic routes of EU from EDA

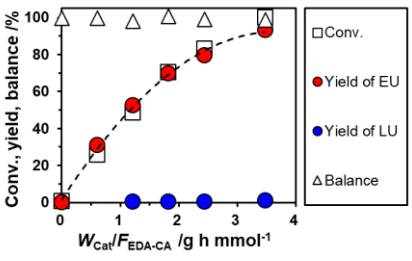

Fig. 2. Effect of contact time on the reaction of EDA-CA over CeO_2 catalyst.
Conditions: 9.2 mol% EDA-CA in EDA, 363 K, TOS 24 h.

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This work was supported financially by NEDO (JPNP18016) and JSPS (18H05247).

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Iron promoted alumina supported nickel catalysts for hydrogenation of carbon dioxide

W. Gac[1,*], W. Zawadzki[1], G. Słowik[1], M. Kuśmierz[1], Z. Surowiec[2], K. Kappis[3]

[1]*Faculty of Chemistry, Maria Curie-Sklodowska University, 3 M. Curie-Sklodowska Sq., 20-031 Lublin, Poland*
[1]*Institute of Physics, Maria Curie-Sklodowska University, 1 M. Curie-Sklodowska Sq., 20-031 Lublin, Poland*
[3]*Department of Materials Science, University of Patras, GR-26504 Patras, Greece*
**wojciech.gac@umcs.lublin.pl*

Keywords: CO_2 hydrogenation, nickel catalyst, iron promoter

Introduction. Carbon dioxide produced during combustion of fossil fuels is commonly perceived as a major contributor to the greenhouse effect. It can be captured and then processed into valuable products, such as methane, methanol or higher hydrocarbons ($CO_2 + 4H_2 \leftrightarrows CH_4 + 2H_2O$). The use of so-called green hydrogen for the hydrogenation of CO_2 additionally allows the storage of renewable energy, as well as improving the efficiency of biomass conversion in biorefineries. The positive effects of the presence of small amounts of iron on the performance of nickel catalysts have been reported for numerous catalytic processes. However, a more comprehensive picture of surface changes of iron promoted alumina supported nickel catalysts in CO_2 hydrogenation is still lacking.

Experimental/methodology. A series of alumina supported catalysts obtained by the application of impregnation method with fixed Ni content (20 wt.% Ni) and different amounts of Fe (from 0 to 10 wt.%) were investigated. The properties of catalysts were studied by the application of versatile experimental methods, including X-ray diffraction, electron microscopy, temperature-programmed reduction, oxidation, H_2 and CO_2 desorption, in-situ DRIFTS CO and CO_2 adsorption/desorption and CO_2 hydrogenation reaction. The state of the catalysts on the different operation stages was investigated by Mössbauer spectroscopy and quasi in-situ photoelectron spectroscopy (XPS). The performance of catalysts in CO_2 hydrogenation reaction was determined using fixed-bed continuous-flow quartz microreactor [1-4].

Results and discussion. An introduction of iron into alumina supported nickel catalysts induced a number of effects, including small changes in the specific surface area and porosity, as well as the formation of mixed oxide species, transformed into the corresponding NiFe alloys under activation conditions. Complex changes in reducibility of oxide phases and the ability of reduced catalysts to form oxide species were evidenced. Although the presence of iron led to a decrease in the active surface area of catalysts, despite a similar nickel content, at the same time an increase in their activity in the CO_2 methanation reaction was observed. It was noticed that the optimal iron content guaranteeing the highest CO_2 conversion under the given conditions depended on the reaction temperature. Thermal analysis, electron microscopy and spectroscopic studies confirmed the formation of NiFe alloys in the catalysts. Their particular forms influenced surface and redox properties of catalysts resulted in the changes of the way of CO_2 activation during hydrogenation reaction, the stability and arrangement of differently coordinated intermediate surface carbonyl groups, formation and subsequent transformation of surface carbonate and formate species.

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Development of a Tailored Multiphase System for the Ru-catalyzed Synthesis of Cyclic Acetals

Niklas Gaelings[1] and Jürgen Klankermayer[1,*]

[1] *RWTH Aachen University, Institute for Technical and Macromolecular Chemistry, Aachen, Germany*
gaelings@itmc.rwth-aachen.de and jklankermayer@itmc.rwth-aachen.de

Keywords: bio-hybrid approach, CO_2 utilization, multiphase catalysis, catalyst recycling

Introduction. In order to reduce carbon dioxide emissions (CO2), a sustainable but also flexible carbon cycle must be made possible in the chemical value chains. In particular, the rapid avoidance of fossil carbon resources and the efficient use of renewable raw materials and energy sources are of the utmost importance.[1,2] Our approach tackles this challenge, by combining different sustainable resource streams into novel bio-based chemicals, namely cyclic acetals (CA), which can be used as solvents, monomers and synthetic fuel (additives).[3,4]

Experimental/methodology. In 2019 our group developed a catalytic system which enables the reaction of CO_2 with hydrogen and bio-based diols for the synthesis of cyclic (e.g. 1,3-dioxolanes, 1,3-dioxanes) and linear acetals.[5] The reaction is facilitated by a homogenous ruthenium catalyst [Ru(triphos)(tmm)] (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, tmm = trimethylene methane) and tailored Lewis acid co-catalyst. A further optimization of the catalytic system led to a restriction of the reaction based on the thermodynamic boundary conditions. Together with the aim of developing an efficient strategy for product separation and recycling of catalysts in terms of a future process, we have transferred the reaction to a multi-phase system.

Results and discussion. Earlier investigations of the mechanism for the Ru(triphos)-catalyzed conversion of CO_2 revealed the importance of an active cationic formate species. A multiphase system was thus targeted, which is composed of an active polar phase with the catalyst and an apolar phase for the cyclic acetal product. Since the liquid substrate for the formation of cyclic acetals is a diol, the substrate was used as polar phase in the multiphase system. The formed cyclic acetals are themselves significantly less polar than the diol and can be extracted in-situ with an apolar solvent. Solvent screening revealed *n*-decane to be the most promising apolar solvent for product extraction. Using a multiphase system consisting of *n*-decane and diol leads to excellent catalyst and co-catalyst retention, while providing an extraction efficiency for the cyclic acetals of up to 85%.

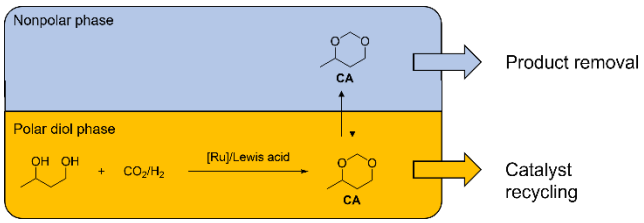

Figure 1: Concept of the tailored multiphase system for the Ru-catalyzed synthesis of cyclic acetals.

Acknowledgments
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Inverse CeO_x/CoO_y catalysts for CO_2 methanation

Yu Gao, Nikolay Kosinov and Emiel Hensen*

Eindhoven University of Technology, Eindhoven, The Netherlands
Email address: y.gao1@tue.nl *e.j.m.hensen@tue.nl*

Keywords: inverse catalysts, CeO_x/CoO_y, CO_2 methanation

Introduction

Growing concerns about global climate make CO_2 capture and (re)utilization of an increasingly attractive opportunity. Ceria-based metals can be used as efficient catalysts for CO_2 hydrogenation due to the unique redox properties of ceria, which include facile formation of surface oxygen vancancies and specific metal-support interactions (MSI).[1] For example, the complex Co-O-Ce interface chemistry including (reverse) oxygen spillover and hydrogen spillover, render Co/CeO_2 catalysts highly active for CO_2 adsorption and activation.[2] Recently, we also reported that constructing Co-O-CoO interface helped to overcome the structure-sensitivity in CO_2 hydrogenation.[3] Herein, we studied inverse CeO_x/CoO_y catalysts in an attempt to maximize interfacial Co-O-Ce sites for optimized CO_2 methanation.

Experimental/methodology

CeO_x/CoO_y catalysts with different Ce mole fractions with respect to Co (0%, 1%, 5%, 10%, 20%, 50%, 90% and 100%) were prepared by flame spray pyrolysis (FSP). H_2-TPR experiments were carried out with a Micromeritics Autoche II 2920 instrument. In situ X-ray absorption spectroscopy (XAS) was performed at the ROCK beamline of Soleil synchrotron in France. CO_2 methanation reactions were performed in a 10-tube parallel high-throughput reactor.

Results and discussion

The CO_2 methanation results for the CeO_x/CoO_y catalysts in Figure 1a shows that the catalytic performance strongly depends on the Ce content and reduction temperature. The highest CH_4 yield was observed for 10%Ce and 20%Ce samples reduced at mild temperature. H_2-TPR profiles (Figure 1b) reveal higher reduction temperature for inverse catalysts as compared with conventional Co/CeO_2, indicating stronger MSI. In situ XAS was used to determine the oxidation state of Co and Ce as a function of the reduction temperature (figure 1c). While metallic Co was formed over pure Co_3O_4 already after reduction at 200 °C, a mixture of Co-CoO was stable in a broad temeprature range for the 20%Ce sample. Ce L_3-edge XANES shows the reduction of Ce^{4+} to Ce^{3+} during reaction for the 20%Ce sample (Figure 1d). This finding indicates formation of abundant oxygen vacancies, facilitating adsorption and activation of CO_2.

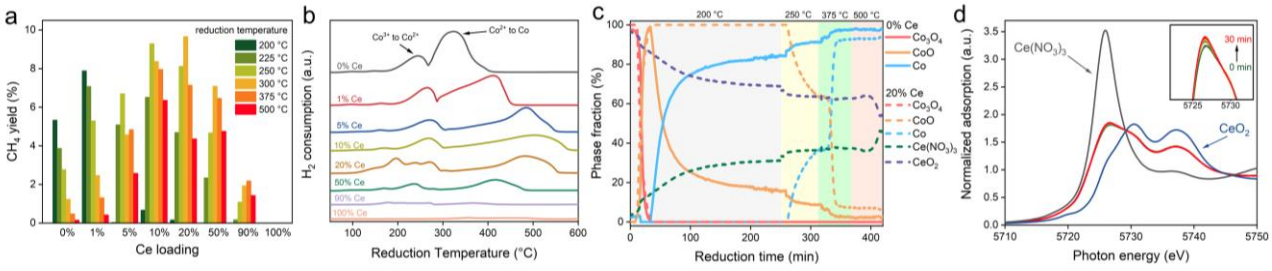

Figure 1. (a) CO_2 methanation over CeO_x/CoO_y catalysts in a flow of CO_2:H_2:He (v/v=1:4:15; total flow 50 ml/min). Samples pre-reduced in 15 vol% H_2 for 4 h at different temperatures; (b) H_2-TPR profiles of CeO_x/CoO_y catalysts; (c) Linear combination fitting of Co K-edge XANES during H_2 reduction for 0%Ce and 20%Ce samples; (d) Normalized Ce L_3-edge XANES of 20%Ce sample during reaction, sample was pre-reduced under 375 °C.

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Isothermal stepwise CO_2 capture-methanation using a dual functional material: effect of the temperature and type of alkaline metal

Enrique García-Bordejé[1], Ana Belén Dongil[2], Jorge Moral[2], José M. Conesa[2], Antonio Guerrero-Ruiz[3], Inmaculada Rodríguez-Ramos[2]

[1]*Instituto de Carboquímica (ICB-CSIC), Zaragoza, Spain,* [2]*Instituto de Catálisis y Petroleoquímica (ICP-CSIC), Madrid, Spain,* [3]*Dto. de Química Inorgánica y Química Técnica, UNED, Madrid, Spain.*

[*]*jegarcia@icb.csic.es*

Keywords: CO_2 capture, methanation, dual functional materials

Introduction. After the pioneering works of Farrauto et al. [1], dual functional materials (DFM) have emerged recently for been studied in the last years for the stepwise isothermal CO_2 capture and methanation. Different combinations of transition metals (Ni, or Ru) and alkali or alkaline earth metals have been explored [2]. For a real application, it is important to assess its cyclic stability at different temperatures under realistic conditions, such as real flue gas, which also contains O_2 and H_2O and other impurities. In addition, it should be born in mind that operating at the lowest temperature as possible is also highly searched for. This would reduce the energy required for heating when the flue CO_2-containing gas is emitted at low temperature or for direct capture from the air (DAC). Herein, we have performed a parametric study of the effect of the reaction temperature on the cyclic performance of DFMs consisting of a metal active in methanation (Ni or Ru) and different alkaline metals (Na, K, Ba) with CO_2 capture ability [3].

Experimental/methodology. Six DFMs were prepared by combining one alkaline metal (Na, K or Ba) and a methanation metal (Ru or Ni) supported on alumina. The loading of alkaline metal was fixed at 10 wt%, the Ru at 3 wt% and Ni at 15 wt% Ni. The DFMs were prepared by sucessive impregnation. In the case of the Ni series, the Ni was added before the alkaline, while, in the case of Ru series, the alkaline was added before the Ru precursor. Finally, the DFMs were treated at 500 ºC first in N_2 and later in H_2 and characterised by CO_2-TPD, TPSR, XRD, XPS and TEM.

Results and discussion. Temperature programed surface reaction (TPSR, Figure 1 a and b) suggested that the COx-adspecies adsorbed at room temperature react at lower temperatures for Ba-contaning DFMs than for the other alkali metals (Na or K). This is an intrisic property of barium since it occurs both for Ni and Ru based sets of DFMs. This highest reactivity for Ba-Ru DFM explains the highest CH_4 productivity (50 µmol g^{-1}) in cycles at the lowest temperature tested of 250 ºC (Figure 1 c). At higher temperatures the highest productivity was provided by Na-Ru DFM (300 µmol g^{-1}) due to the larger CO_2 capture capacity.

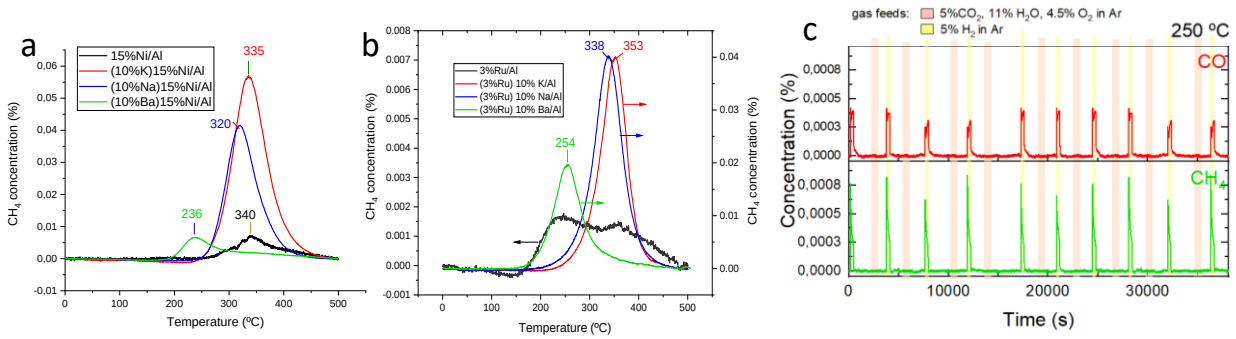

Figure 1. TPSR experiment for DFMs of the Ni series (a) and of the Ru series (b). Cyclic CH_4 and CO production during hydrogenation of previously captured CO_2 from a gas containing 5%CO_2, 11%H_2O and 4.5% O_2 in Ar.

Acknowledgments

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Catalyst Design of CO_2 Hydrogenation and Off-gas Upgrading

K. An[1*]
[1]*Ulsan National Institute of Science and Technology (UNIST), Ulsan, South Korea*
[*]*kjan@unist.ac.kr*

Keywords: CO_2 Hydrogenation, Off-gas upgrading, Hydroformylation, Single atom catalyst.

Introduction. The steady increase of CO_2 in the atmosphere owing to the excessive use of fossil fuels is seriously threatening the future of humankind by accelerating climate change. Among the proposed a carbon capture and utilization options, catalytic CO_2 hydrogenation is attractive because the process is very similar to the well-established CO hydrogenation. The CO_2 hydrogenation process usually involves two consecutive steps: the reverse water−gas shift (RWGS) and subsequent CO hydrogenation reactions. In CO_2 hydrogenation over Fe-based catalysts, the Fe_3O_4 phase catalyzes the RWGS reaction, and its reduced form, the Hägg iron carbide (χ-Fe_5C_2) phase, provides active sites for CO hydrogenation and chain growth. CO_2 hydrogenation can produce a wide variety of products, including methane, light olefins, and heavier (C_{5+}) hydrocarbons. Gaseous by-products produced by CO_2 hydrogenation reaction contain large amounts of light olefins and paraffins (C_2–C_4). Hydroformylation not only simplifies the separation process by converting only olefins to liquid aldehydes and alcohols but also produces high-value-added chemicals with high commercial value. The newly developed Rh/CeO_2-Al_2O_3 single atom catalyst was applied to upgrade the off-gas generated from CO_2 hydrogenation by performing hydroformylation using a olefin/paraffin mixed gas.

Results and discussion. Monodisperse nanoparticles (NPs) of $CoFe_2O_4$ were synthesized as efficient catalyst precursors for CO_2 hydrogenation to produce high value-added C_2–C_4 olefin products. The resulting Na-promoted $CoFe_2O_4$ catalysts supported on carbon nanotubes (Na−$CoFe_2O_4$/CNT) exhibited high CO_2 conversion (~34%) and light olefin selectivity (~39%), outperforming other reported Fe-based catalysts under similar reaction conditions. Their performance was superior to that of single-metal NP catalysts (Na−Fe_3O_4/CNT and Na−Co/CNT) and a physically mixed (Na−Fe_3O_4 + Co)/CNTcatalyst.

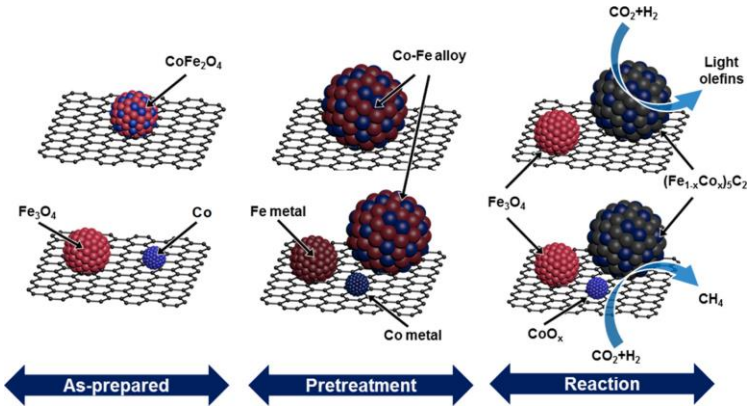

Fig. 1. Phase Transformations of $CoFe_2O_4$ NP catalysts during CO_2 hydrogenation.

Rh/CeO_2-Al_2O_3 single atom catalsyts were designed with a tailored Rh electron density as a function of Ce concentration. When 2 wt% of Ce was supported into the Al_{penta}^{3+} sites of γ-Al_2O_3 and reduced at 600 °C, Ce^{3+} species with abundant oxygen vacancies promote the formation of highly dispersed Rh single atoms. The highly optimized Rh/CeO_2-Al_2O_3 single atom exhibited the highest hydroformylation activity comparable to homogeneous Wilkinson's catalyst. Based on the combined analytical results and theoretical calculations, it was demonstrated that the higher the surface Ce^{3+} ratio, the higher the Rh electron density and the lower the CO adsorption strength, which resulted in the high catalytic activity during hydroformylation.

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Modeling and simulation of a non-isothermal fixed-bed reactor for CO_2 methanation and validation with experimental data

E. Gómez Bravo*, J.A. González-Marcos, J.R. González-Velasco, B. Pereda-Ayo

Departamento de Ingeniería Química, Facultad de Ciencia y Tecnología, Universidad del País Vasco UPV/EHU, 48940-Leioa, España
**elena.gomez@ehu.eus*

Keywords: Methanation, Carbon dioxide, Hydrogen, Renewable energy, Reactor design

Introduction. The CO_2 hydrogenation ($CO_2+4H_2 \leftrightarrows CH_4+2H_2O$) allows the conversion of renewable H_2 into an easily storable and transportable carbon neutral synthetic natural gas (CH_4). The high exothermicity of the reaction can be an advantage to speed up the reaction kinetics, but an excessive increase of temperature can lead to thermodynamic limitations and accelerate catalyst aging [1]. In this context, reactor design assisted by modeling can be a very useful tool for the construction of large-scale methanation reactors with efficient heat management [2]. Thus, the aim of this work is to develop and validate a mathematical model that accurately predicts the reactor's performance under different operating conditions.

Experimental/methodology. Catalyst composition was 5%Ni/Al_2O_3. First, a kinetic study was carried out in an isothermal microreactor with 0.5 g of catalyst diluted with 50% quartz. Experiments were carried out at different temperatures (275-350 °C) with different spatial times (W/F_{A0}=2.5-10 g s mol^{-1}). Afterwards, experiments were carried out in a quartz reactor (D=9mm; L=25mm) loaded with 1 g of catalyst and placed inside a tubular furnace. The feed gas flowrate was 100 mL/min of CO_2 with a H_2/CO_2 ratio of 4. Temperature was measured by 6 thermocouples equidistantly placed along the reactor axial coordinate. Gas products at reactor outlet were measured by gas chromatography. Mathematical models with different complexity were built in Matlab, starting from 1D plug-flow (PF) pseudo-homogeneous model, to 2D heterogeneous models, which account for mass and energy transport in both the axial and radial coordinates.

Results and discussion. The reaction rate derived from the kinetic analysis was implemented in developed models to simulate the non-isothermal reactor performance. Figure 1 shows the experimental CO_2 conversion at the reactor outlet and temperature profile along the reactor with simulated profiles using 1D pseudo-homogeneous models with ideal or non-ideal PF, when gases were fed to the reactor at 300 °C. As can be observed, the ideal PF model is not able to describe experimental data. The consideration of mass and energy transport in the axial coordinate by the non-ideal PF model flattens conversion and temperature profiles with respect to ideal PF model. Heat is dissipated by conduction from the hot spot, which increases the temperature at the reactor entrance (520 °C) and promotes CO_2 conversion. After a hot spot (560 °C) located near the reactor entrance (2.5 mm), the reactor dissipates the heat of reaction to furnace surroundings, which reduces temperature and allows the CO_2 conversion to grow. CO_2 conversion at the reactor outlet and temperature profile are accurately described by the non-ideal PF model for estimated values of k=6 W/(m·K), $D=9\cdot10^{-3}$ m^2/s and U=100 $W/(m^2\cdot K)$. At the operating conditions, heterogeneous models do not predict significant temperature and concentration gradients among gas and solid phases or inside the catalyst particle.

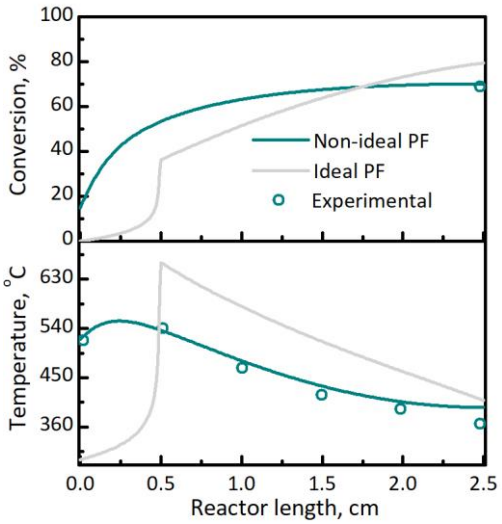

Figure 1. CO_2 conversion at reactor outlet along with temperature profile.

Acknowledgments. Ministerio de Ciencia e Innovación (PID2019-105960RB-C21, FPU 20/06668)

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Boosting the catalyst stability and activity of Ni/MgO-Al_2O_3 with different complexing agents for dry reforming of methane

Santiago S. Gonzalez, Hanan Atia*, Nils Rockstroh, Hendrik Lund, Stephan Bartling, Sebastian Wohlrab, Udo Armbruster

All at Leibniz-Institut für Katalyse e. V., Albert-Einstein-Str. 29a, 18059 Rostock, Germany

**Hanan.Atia@catalysis.de*

Introduction Reaching the industrial maturity of the dry reforming of methane (DRM; CH_4+CO_2 □ $2H_2+2CO$, ΔH=+247 kJ/mol) is challenging due to the lack of effective catalysts being resistant towards sintering and coke formation at the required high temperatures [1]. Closing this gap would possibly rely on the synthesis of robust catalyst based on cheap and abundant elements (Ni, Co) via up-scalable techniques. Hence, we explored the effects of assisting the synthesis of low-loading Ni-based (2.5 wt.%) catalysts with different organic ligands (L) to improve the catalyst stability and activity towards DRM.

Experimental In presence of the ligands glycine (Gly), citric acid (CA), ethylenediaminetetraacetic acid (EDTA) and pentetic acid (DTPA) at L/Ni=1.5, low Ni loads (2.5 wt%) were deposited on MgO-Al_2O_3 (50:50 wt%) via wet impregnation and subsequent calcination in static air at 800 °C for 6 h. The fresh, *ex-situ* reduced and spent catalysts were characterized (XRD, TPR, XPS, etc). The catalyst tests were performed in fixed-bed continuous flow quartz reactors with stoichiometric feeds ($CH_4/CO_2/N_2$ = 45:45:10 vol%) at high flow rate (GHSV = 170 L/(g_{cat}·h)). Prior to testing, the catalysts (50 mg) were *in-situ* reduced (700 °C for 1.5 h under H_2). The temperature program followed the order 750-700-650-600-750 °C, 4 h each hold. The product gas was analyzed with GC-BID. The outperforming catalysts were subjected to long-term runs at 600 °C.

Results and discussion Assisting the catalysts' synthesis with different ligands affected their physicochemical properties and consequently, their performance. The TPR profiles (Figure 1a) showed that the Gly-assisted catalyst was endowed with the highest reduction temperature (T_{red}=930 °C), and thus, the strongest metal-support interaction (MSI) among the series. These observations pointed out to an enhanced Ni dispersion [2]. In terms of activity, the Ni(Gly) catalyst stood out at all temperatures. Special attention was paid to the lower temperature range (T=600-650°C), as the reaction is far from thermodynamic limitations but kinetically controlled and at the same time prone to coke formation [3]. Ni(Gly) showed X_{CH4}=41% and X_{CO2}=57% (Figure 1b and c, respectively) at 600 °C, forming 4.4 wt% coke after 20 h on stream (TOS). Even though Ni(EDTA) produced less coke (1.8 wt% C) than Ni(Gly), the activity of the former (X_{CH4}=35% and X_{CO2}=52%) was inferior to that of the latter. The above observations suggest that the strong MSI and presumably higher Ni dispersion of the Ni(Gly) catalyst play a crucial role for its notable performance and coke resistance. Within 20 h at varying temperatures and coke formation, the catalysts slightly deactivate.

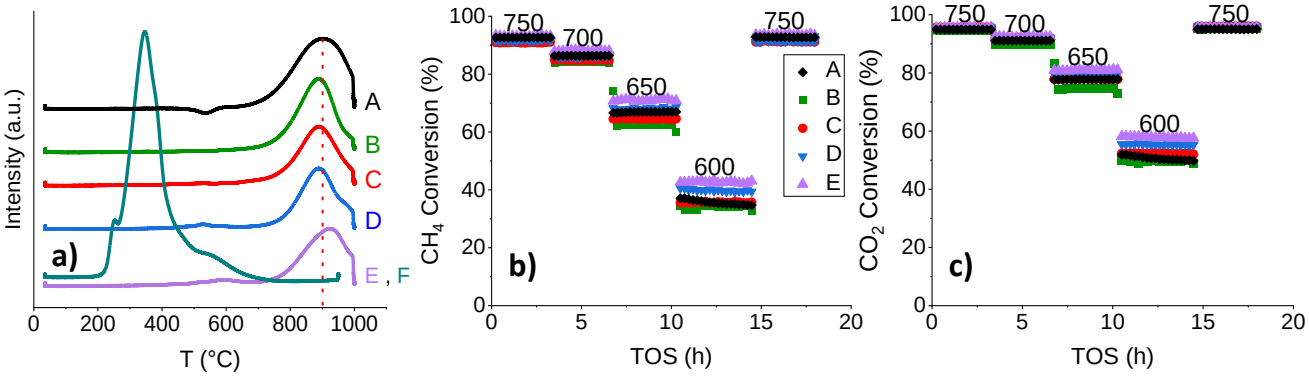

Figure 1. a) Temperature-programmed reduction profiles. Conversions with TOS for b) CH_4 and c) CO_2. The numbers on the top of each step indicates the temperature (in °C). Reaction conditions: P = 1 bar, m_{cat} = 50 mg, GHSV = 170 L/(g_{cat}·h), $CH_4/CO_2/N_2$ = 45:45:10 vol%. A = Ni/$Mg_{1.3}AlO_x$, B-E = Ni(L)/$Mg_{1.3}AlO_x$ (L= B: CA, C: EDTA, D: DTPA and E: Gly), F = NiO.

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Effect of nickel nanoparticle size over silica based catalysts for methanation reaction

Manon Grégoire[1*], Carmen Ciotonea[1, 2], Sébastien Royer[2], Sharad Gupta[1], Edmond Abi-Aad[1], Christophe Poupin[1]

[1] *Univ. Littoral Côte d'Opale, UR 4492, UCEIV, Unité de Chimie Environnementale et Interactions sur le Vivant, F-59140, Dunkerque, France*
[2] *Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, 59000, Lille, France*
[*] *manon.gregoire@univ-littoral.fr*

CO_2 is one of the main greenhouse gases thus reducing its emissions is an important issue. The methanation process, which results in the methane production through CO_2 reduction is a potential method to decarbonate industrial effluents. In a Power-to-Gas development, CO_2 methanation is a very promising way to use and storage H_2, produced by renewable energy into CH_4 for which storage and distribution network already exist. In the literature, supported catalysts based on noble metals (Ru, Rh) and on transition metals (Ni, Co) are frequently reported for the use over methanation reaction [1]. In order to obtain efficient catalysts, with similar properties as the noble based catalyst, it is important to produce materials with highly dispersed nanoparticles (NPs) of small sizes, together with improved thermal stability. In methanation reaction, Ni NPs size has a strong influence on the activity and the selectivity towards CH_4 production [2]. The aim of this study is therefore, to finely tune NPs size and to confine Ni NPs preferentially either into micro- or mesoporosity within a hierarchical silica type SBA-15. Controlled size nanoparticles generation will allow to investigate the evolution of the activity and selectivity for CO_2 methanation.

In the present study, a series of materials containing 10 wt.% Ni were prepared, with the aim of producing NPs of sizes ranging from 3 nm to 12 nm, using suitable methods: Melt Infiltration (MI) of nitrate precursor onto P123-SBA-15 (Ni/MI) and Incipient Wetness Impregnation (IWI) on SBA-15 (Ni/IWI). IWI was also used to prepare a reference catalyst impregnated on commercial SiO_2 (Ni/SiO_2). The calcined and activated (H_2) materials were characterized by XRD, N_2-physisorption S/TEM- coupled with EDX mapping, and H_2-TPR.

XRD confirms the presence of 9 nm crystallites for Ni/IWI and crystallites smaller than 3 nm for Ni/MI. In addition, microscopy confirms the presence of highly dispersed particles into the SBA-15 porosity (Fig 1a). Ni/SiO_2 is revealing presence of large NPs of > 12 nm, probably located at the external surface of the silica. NPs presence into microporosity is revealed by N_2 isothermes. TPR indicated the presence of NPs confined in Ni/IWI SBA-15 porosity, and NPs in strongly interaction with silica for Ni/MI. The evolution of the catalytic properties was assessed for the reduced materials over methanation reaction (Fig 1b). Results collected are proving benefit effect of 3 nm NPs by comparison to larger NPs sizes of 9 nm or 12 nm. Ni/MI has superior catalytic activity at low temperatures (yield of CH_4 = 93% at 360 °C) due to a higher covering with active sites of the smaller NPs.

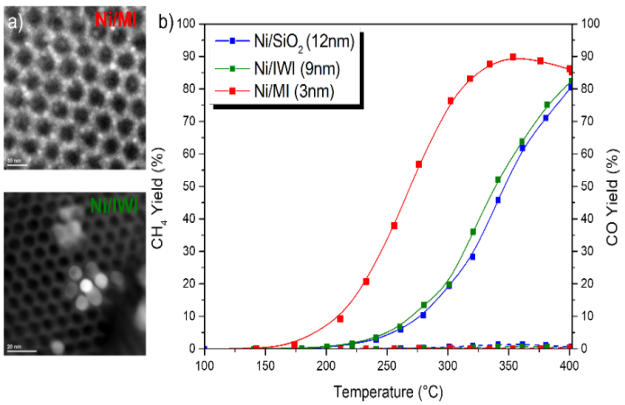

Figure 1 : **a) HRTEM-HAADF for reduced Ni/IWI and Ni/MI b) CH_4 and CO yield of Ni/IWI, Ni/Mi and Ni/SiO_2**

In conclusion, by controlling Ni based catalysts NPs size the selectivity is oriented toward the production of methane with high yield at 360 °C with high thermal stability.

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Recyclable hybrid catalytic systems for the synthesis of cyclic carbonates

V. Campisciano[1], A. Morena[1,2], L. Valentino[1], A. Comès[2], L. Fusaro[2], A. Santiago-Portillo[2], L.F. Liotta[3], F. Giacalone[1], C. Aprile[2], M. Gruttadauria[1*].

[1]*Department of Biological, Chemical and Pharmaceutical Sciences and Technologies- University of Palermo, Viale delle Scienze,Ed.17, Palermo I-90128, Italy*
[2]*Unit of Nanomaterials Chemistry, Department of Chemistry, NISM, University of Namur, 61 rue de Bruxelles, 5000 Namur, Belgium*
[3]*Istituto per lo Studio dei Materiali Nanostrutturati ISMN-CNR, via Ugo La Malfa 153, 90146 Palermo(Italy)*
[*]*michelangelo.gruttadauria@unipa.it*

Keywords: carbon dioxide fixation, bifunctional catalyst, Al-porphyrin, silsesquioxanes, carbon nanotubes

Introduction. Valorization of CO_2 as C1 building block in chemical production is a topic of great interest. Then, synthesis of cyclic carbonates via addition of CO_2 to epoxides has received a paramount attention and, in this context, we have been involved in the development of hybrid catalytic systems based on carbon nanoforms or polysilsesquioxanes (POSS) coupled with covalently linked poly-imidazolium salts with or without supported Lewis acids as co-catalytic species.[1-4]

Experimental/methodology. Catalytic experiments were carried out using a Cambridge Design Bullfrog batch reactor equipped with temperature control and mechanical stirring. In each test, the catalyst and the proper epoxide (24 mL) were added to a Teflon vial and then the reactor was closed. After passing a flow of N_2 for 10 min and loading 25 bar of CO_2, the system was left to react at the target temperature reached by a ramp of 5 °C/min. In selected cases, a refill of CO_2 was carried out during the experiment. In these cases, the initial pressure of CO_2 was never overpassed. After the proper reaction time (3 h or 24 h), the reactor was cooled down to room temperature, depressurized and, then, the catalyst was recovered from the reaction mixture by centrifugation. Each catalyst was dried overnight under vacuum at 60 °C prior to the catalytic test.

Results and discussion. Here we report our studies using two different supports (POSS or CNT) modified only with polyimidazolium salt having halides as counterions or modified with polyimidazolium salt/aluminium-porphyrin complex. These materials were prepared following a straightforward synthetic procedure based on polymerization of suitable precursors, then, they were fully characterized. The synergic cooperation between catalyst and co-catalyst moieties was observed when halide/Lewis acid were present. All the materials proved to be recoverable and reusable with high TON, TOF and Productivity values. A peculiar behaviour was observed in the case of polyimidazolium-modified carbon nanoform-modified catalysts that showed an increased activity after recycling, ascribed to a change in their morphology. [3,5].

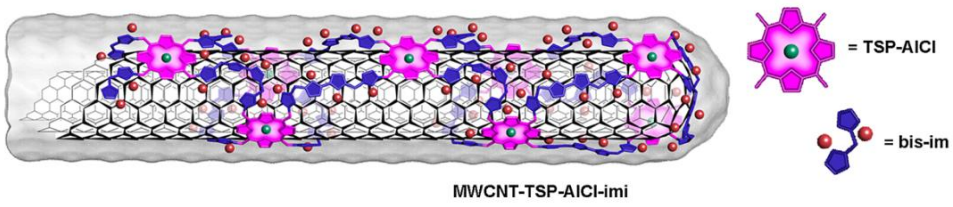

Figure. Schematic representation of Al-porphyrin/polyimidazolim salt supported on MWCNT.

Acknowledgments
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Biogas upgrading through enhanced CO_2 methanation in fluidized bed

I. de Matías, P. Durán, V. D. Mercader, E. Francés, J. Herguido*, J. A. Peña

[1]*Catalysis, Molecular Separations and Reactor Engineering Group (CREG), Aragón Institute of Engineering Research (I3A), Universidad Zaragoza, Zaragoza (Spain)*
**jhergui@unizar.es*

Keywords: methanation, biogas, sorption enhancement, power to gas, fluidized bed

Introduction. This work studied the potential application of *Power to Gas Technologies* (*PtG*) for biogas upgrading assisted by water removal. *PtG* can transform gas flows rich in CO_2 (such as biogas 70% CH_4 and 30%CO_2) into methane through Sabatier's reaction. The set-up chosen for the methanation was a fluidized bed reactor filled with a mixture of lab-made Fe-Ni/γ-Al_2O_3 catalyst [1] and zeolite 5A as water adsorbent. Fluidized-bed reactor was proposed as alternative to conventional fixed-bed reactors because of its thermal properties, avoiding the generation of "hot spots". In order to improve the fluidization of zeolite 5A (d_p: 200-250 µm), gamma alumina particles (d_p: 100-160 µm) were also included as fluidizer assistant. It was found an accurate isothermal behavior, elevated conversions of CO_2 during the intensification period and high selectivity to methane.

Experimental/methodology. Experimental set-up consisted in a fluidized-bed reactor of 7 cm (bed length in repose) thermally monitoring by 5 thermocouples along the bed length (during reaction). Gas inlet was introduced at atmospheric pressure and 570 ml/min STP, in order to ensure the total fluidization. Feeding rate was the stoichiometric CO_2:H_2 (4:1) and for biogas upgrading the rate CH_4:CO_2 was a representative sweetened biogas concentration (7:3). Temperature influence in the methanation reaction was tested at different temperatures (250-400°C).

Results and discussion. Results from the methanation cycles are showed in Figure 1, were M are the methanation cycles. Between methanations inert gas was introduced in order to regenerate the zeolites, also between M3 and M4 a reactivation step was performed. It was found the positive effect in the CO_2 conversion due to including zeolite 5A in the reactor bed (Table 1). Zeolite enhances the first moments of the methanation by its water removal properties, shifting the equilibrium to the products. After the zeolite is saturated the intensification behavior is reduced until showing a stationary conversion value (Fig. 1).

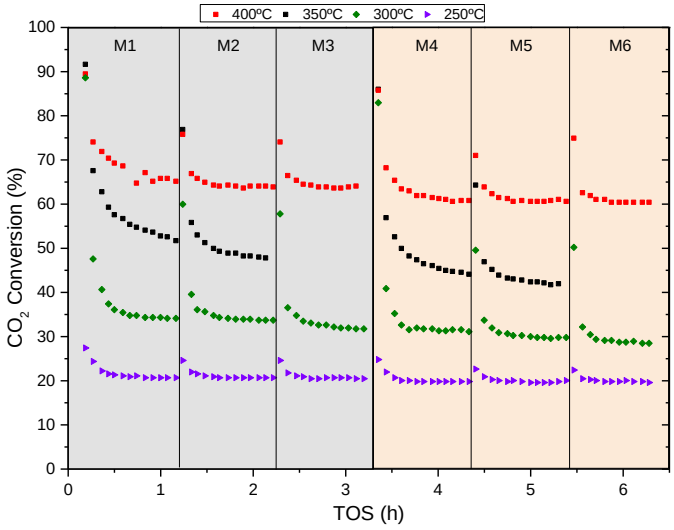

Figure 1. CO_2 conversion *vs.* time-on-stream.

Table 1. Process intensification (%), as relative improvement in terms of CO_2 conversion, for each temperature and methanation step.

T(°C):	250	300	350	400
M1	4.53	13.54	12.37	6.19
M2	2.11	7.22	7.91	2.33
M3	2.35	7.51	-	2.08
Oxidation (O_2) + Regeneration (H_2)				
M4	2.75	13.32	11.89	5.11
M5	2.32	6.55	6.49	1.89
M6	2.82	7.05	-	2.08

Acknowledgments
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Catalyst supports based on ceria-praseodymia as oxygen carriers for applications in methane reforming reactions.

L. Herráez-Santos*, A. García-García

Grupo MCMA, Departamento de Química Inorgánica e Instituto Universitario de Materiales, Universidad de Alicante, Sant Vicent del Raspeig, Alicante, SPAIN

*lucia.herraez@ua.es

Introduction. Both the catalytic reaction of dry methane reforming (DRM) and the reforming reaction of methane with steam using an oxygen carrier (Chemical Looping Steam Methane Reforming), require catalyst supports with very labile oxygen, which actively participates in these reactions, or potentially gasify unwanted carbonaceous deposits that are generated during the dry reforming reaction [1]. In this sense, the development of supports based on ceria-praseodymia mixed oxides with a known high reducibility and capacity to generate a high population of oxygen vacancies and, therefore, with high ability to store and release oxygen, seems appropriate in this context. These oxides will be employed as supports for Ni and Co active phases in order to conduct a preliminary study related to the catalytic dry reforming of methane.

Experimental/methodology. As a preliminary study**,** several supports based on ceria-praseodymia have been designed (exploring the full range of composition in Ce/Pr) and characterised to analyse their lattice oxygen under different reaction atmospheres (H_2, He and in contact with a carbonaceous compound, which is used as a test reaction to simulate the carbonaceous deposit created under real reaction conditions). The support with the best characteristics was impregnated with nickel and/or cobalt precursors (5% w/w) and subsequently tested for the dry reforming of methane reaction.

Results and discussion. Pure praseodymia presents the best features to be used as a support of catalysts in the selected reaction (see Table 1).

Table 1. Comparison of the level of non-stoichiometry generated after the reduction in different atmospheres.

Support	[1]δ	[1]Formula after reduction	[2]δ	[2]Formula after reduction
PrO_2	0,261	$PrO_{1,74}$*	0,332	$PrO_{1,67}$*

[1]No stoichiometry and formula reached after reduction under He atmosphere.
[2]No stoichiometry and formula reached after reduction under H_2 atmosphere.
*Values close to the theoretical value of the Bevan Cluster ($PrO_{1,71}$-PrO_2).

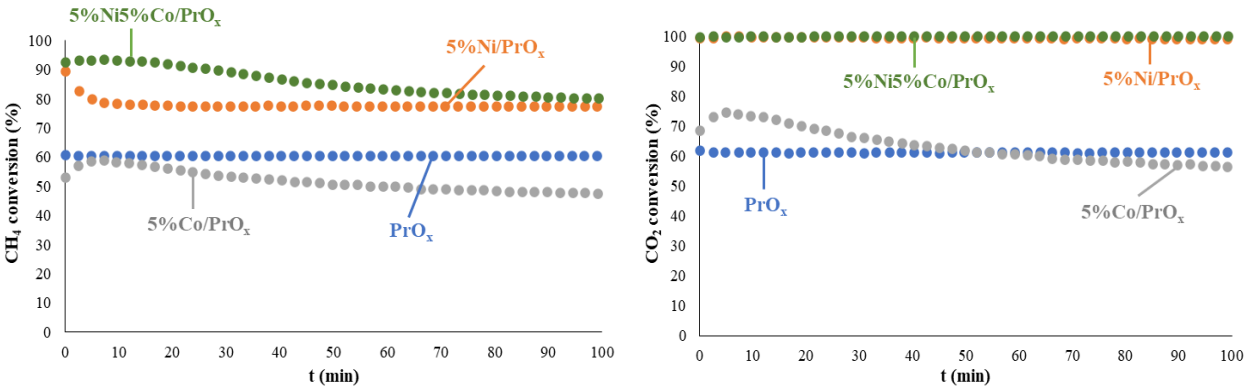

Figure 1. CH_4 and CO_2 conversions versus time. (Conditions of the catalytic tests: pre-reduction under 5%H_2/He at 500ºC; flow rate = 40 mL/min and reaction conditions: CH_4/CO_2/He (4/4/92) at 750ºC, with a flow rate of 60 mL/min, 50 mg catalyst/100 mg SiC).

As can be seen in Figure 1, pure praseodymia seems to be a promising support for this catalytic reaction and the designed catalysts (especially those containing Ni) are characterised by high activity and selectivity, reaching 100% of CO_2 conversion.

Acknowledgments

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UiO-66 supported Cu catalysts for CO_2 hydrogenation to methanol.

Zonggao Hu[1*], N. F. Dummer[1], K. J. Aggett[1], N. Lawes[1], I. E. Gow[1], L. R. Smith[1], J. S. Hayward[1], T. E. Davies[1], D. J. Morgan[1], M. Bowker[1], S. H. Taylor[1], G. J. Huthchings[1]

[1]*Max Planck–Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, United Kingdom*
[*]*Corresponding Author's E-mail: HuZ13@cardiff.ac.uk*

Keywords: metal-organic frameworks, Cu catalysts, CO_2 hydrogenation to methanol

Introduction. Thermocatalytic CO_2 hydrogenation to value-added chemicals and fuels such as methanol is one of the promising approaches for reducing CO_2 emissions. As a frontier of catalysis, heterogeneous single-site catalysts have shown excellent catalytic performance in many applications.[1] However, their applications in thermocatalytic CO_2 hydrogenation to methanol are rarely reported.[2] In terms of preparing single-site catalysts, MOFs (metal-organic frameworks) with tunable structures, morphologies and compositions hold great potential.[1] Cu-based nanoscale catalysts have been extensively studied due to its low cost and the effective methanol synthesis from CO_2 hydrogenation, but still suffer from insufficient activity and stability.[3] Therefore, there is a need to deeply study MOFs-based Cu single-site catalysts for methanol synthesis from CO_2 hydrogenation.

Experimental/methodology. Zr-based MOF UiO-66 samples were prepared by a solvothermal method. Zirconyl chloride octahydrate, terephthalic acid and acetic acid were dissolved in N,N-dimethylformamide (DMF), and then the mixture was sealed and heated for 18 h. The products are denoted as "UiO-66-L/Mx-AAy-Tz" where x is the molar ratio of ligand to metal precursors (L/M) in synthesis; y represents the amount of acetic acid (AA) added; z stands for synthetic temperature (T).

Cu catalysts supported on UiO-66 or UiO-66-derived ZrO_2-C were synthesized by an impregnation and heat treatment method. UiO-66 was added to the solution containing $CuCl_2{\cdot}2H_2O$ dissolved in DMF and then the mixture was sealed and heated at 90 °C for 18 h. The resultant $CuCl_2$/UiO-66 samples were heated under 5% H_2/Ar at 300 °C for 3 h or N_2 at 600 °C for 3 h to form Cu/UiO-66 or Cu/ZrO_2-C, respectively (UiO-66 in Cu/UiO-66-1 and Cu-ZrO_2-C-1 is UiO-66-L/M1-AA50-T90, while for Cu/UiO-66-2 and Cu-ZrO_2-C-2 is UiO-66-L/M1-AA100-T90). The catalytic performance of these catalysts was tested for CO_2 hydrogenation at 230-250-270 °C.

Results and discussion. XRD, SEM, TGA and N_2 adsorption/desorption isotherms results show that the crystalline, size, morphologies, and defects of UiO-66 can be tuned by changing the synthetic conditions. Among four catalysts, Cu/UiO-66-2 showed both highest methanol selectivity (52%) and productivity at 270 °C of 1324 $mmol_{MeOH}$ h^{-1} kg^{-1} with *ca*. 1 wt. % Cu loading of 0.2 g used in the reaction.

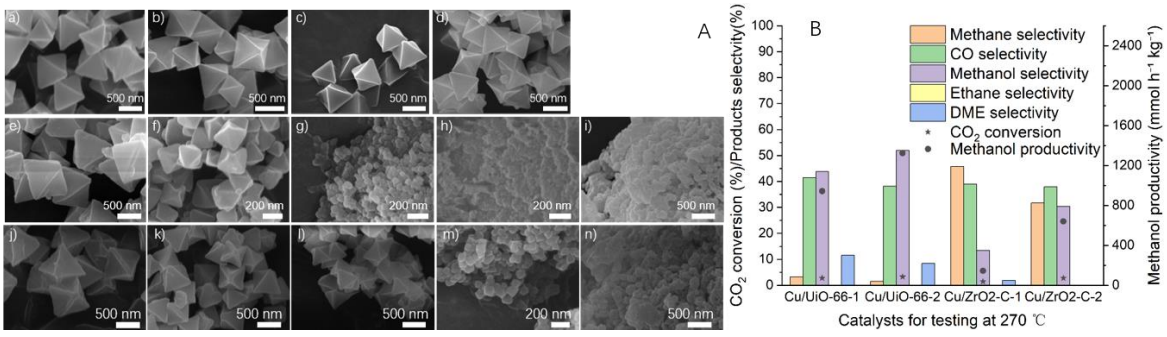

Figure 1 (A) SEM images of UiO-66 samples under different conditions: (a-d) a, b, c, and d represent 120, 110, 100, 90 °C (L/M=4.6, AA=125 mL); (e-i) e, f, g, h, and i with 100, 75, 50, 25, 0 mL acetic acid (L/M=4.6, T=90 °C); (j-n) j, k, l, m and n with 100, 75, 50, 25, 0 mL acetic acid (L/M=1, T=90 °C); (B) Catalytic results of different catalysts at 270 °C, 20 bar, 30 ml/min (CO_2:H_2:Ar:N_2 20:50:5:25), 0.2 g catalyst.

Acknowledgements

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Investigating the influence of ionic liquids on the visible-light induced photoelectrochemical reduction of CO_2

B. Hulaj[1*], D. Apaydin[2], K. Bica-Schröder[1]

[1]*Institute of Applied Synthetic Chemistry, Technische Universität Wien, Vienna, Austria*
[2]*Institute of Materials Chemistry, Technische Universität Wien, Vienna, Austria*
[*]*blete.hulaj@tuwien.ac.at*

Keywords: ionic liquid, carbon dioxide valorization, photoelectrochemistry, polymer

Valorization of carbon dioxide is a promising approach that could simultaneously address multiple global issues. Reduced emission to the atmosphere signifies minimized impact on global warming, while the abundant, non-toxic, and renewable nature of CO_2 is aligned with the vision for sustainable processes. Nevertheless, the viability of this option requires an efficient catalytic system since the reduction of this greenhouse gas to value-added chemicals is hindered by a high thermodynamic and kinetic barrier [1].

Research on visible light photocatalyzed carbon dioxide reduction revealed that photocatalytic systems consisting of a ruthenium-based photosensitizer and a rhenium-based photocatalyst exhibit high selectivity for carbon monoxide formation. Additionally, electrochemical reduction provides the possibility to control the process by varying the applied potential in a compact set-up [1,2]. Photoelectrochemical reduction of carbon dioxide combines photo- and electrocatalysis towards mutually beneficial interactions. The applied potential can improve the separation of charges, while light irradiation reduces the required overpotential of the electrocatalytic process. Hence, the photocathodes act as both, catalyst and light harvester. Furthermore, past research demonstrated the advantages of ionic liquids as cooperative media, due to their ability to solubilize large concentrations of carbon dioxide and, in specific instances, minimize the required applied potential for the reduction [1]. Consequently, we aim to combine the advantages of these methods into a photoelectrochemical set-up and investigate the influence of ionic liquids on the reduction efficiency of carbon dioxide to carbon monoxide.

Preliminary UV-Vis spectroscopy data, as shown in figure 1, have already confirmed that the synthesized materials combining rhenium, ruthenium and an ionic liquid in a polymer framework show high correlation with reported absorbance values for the corresponding monomers (i.e., $[Ru(bpy)_3][PF_6]$, $Re(bpy)(CO)_3Cl$, and EMIM Br), enabling photocatalytic reduction in the visible-light region above 445 nm [3]. By fabricating a conductive polymer film of these components on a cathode, the reduction can be further enhanced through the applied potential in a photoelectrochemical set-up to determine the optimal reaction conditions.

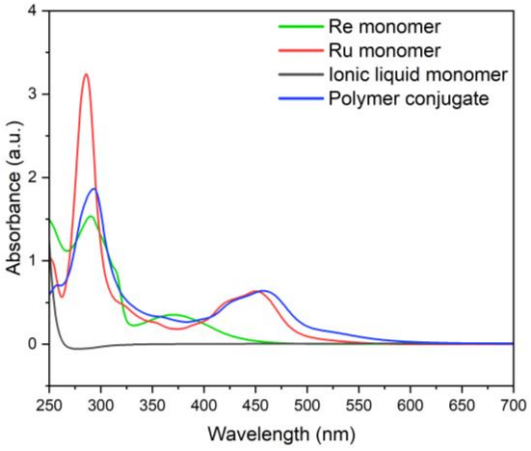

Figure 1 UV-Vis spectra of a Re, Ru and ionic liquid monomer, and a polymeric conjugate of the three monomers

Acknowledgments
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Ni composite catalysts on CeLaCuO/SBA-15 support towards dry reforming of methane (DRM)

Aseel G. S. Hussien[1,2], Aasif A. Dabbawala[1,2], Dalaver H. Anjum[3], Nikolaos D. Charisiou[4], Maria Goula[4], Kyriaki Polychronopoulou [1,2,*]

[1]*Department of Mechanical Engineering, Khalifa University of Science and Technology, Abu Dhabi 127788, United Arab Emirates*

[2]*Center for Catalysis and Separations, Khalifa University of Science and Technology, Abu Dhabi 127788, United Arab Emirates*

[3]*Department of Physics, Khalifa University of Science and Technology, Main Campus, P.O. Box 127788, Abu Dhabi, United Arab Emirates*

[4]*Department of Chemical Engineering, University of Western Macedonia, Koila, 50100 Kozani, Greece*

[*]*kyriaki.polychrono@ku.ac.ae*

Keywords: Doped ceria, DRM, lattice oxygen, coking, Ni supported catalyst, SBA-15

Introduction: The renewed intrest in dry reforming of methane (DRM: $CH_4+CO_2 \leftrightarrow 2CO+2H_2$) reaction is linked to the production of synthesis gas with CO/H_2 of unity, which can be used to produce high value-added chemicals and fuels via Fischer-Tropsch (FT) process [1-3]. Additionally, DRM provides a direct route for biomass (CH_4: 50–70 % and CO_2: 25–50 %). The lack of an economically feasible, stable, and coke resistance catalyst has hinderend the industrialization of this process. Ni-based catalysts offer a cheap alteranative compared to the noble-metal based counterparts as they have a similar catalytic activity. However, coke formation through CH_4 decomposition and CO disproportionation are the main reaction routes of carbon formation during DRM [1,3]. Our previous study on Ni/Ce-M-10Cu-O (M = La or Sm) synthesized via enhanced microwave (EMW) synthesis showed that Ni/Ce-La-10Cu catalyst exhibited the lowest carbon formation [6].

Experimental: In this study, SBA-15 was used as a carrier of the ceria-doped oxide with different loadings of Ce-La-10Cu-O (X=0%, 10%, 20%, 30% and 40%) and finally the surface was decorated with 5 wt.% Ni. SBA-15 was utilized to highly disperse the ceria and tune its interface with Ni metal, since SBA-15 presents a high internal surface area (400-900 m^2/g) and is predominantly mesoporous silica sieve with hexagonal pores and a pore diameter that ranges between 5-15 nm [7].

Results and discussion: A suite of analytical techniques was used to get an insight on the catalyst structure and undertand how this links with the performance. Powder XRD, BET, HAADF-STEM, SAED, EELS, elemental mapping, Raman, CO_2-TPD, H_2-TPR, H_2-TPD and Solid State NMR were employed to characterize the complex multi-elemental composition of the catalysts. XRD and Raman results (X>20%) confirmed the cubic flourite stucture of ceria and the mesoporous structure of SBA-15 as well as the presence of oxygen vacancies in the catalyst. Solid state NMR was used to probe the formation of Si-O-M bond and the anchoring of the ceria phase onto the silica matrix. H_2-TPD studies showed that 5%Ni/30%CeLa10Cu-SBA-15 catalyst had the highest Ni dispersion (%) and the smallest Ni size amongst all the catalysts; this corroborates with the higher CO_2 and CH_4 conversion rates compared to the rest X% CeLa10Cu promoted catalysts. HR-TEM showed the dispersion of Ni and Ce-La-10Cu-O, some areas exhibited Cu exsolution resulting in NiCu alloying specially in the case of 30% and 40% CeLa10Cu loading. The catalyst with the highest CeLa10Cu loading (40%) showed the highest coke balance (%) after 12h time on DRM stream, which can be linked to the oxygen storage capacity of ceria that gasifies carboneous species. However, it exhibited the lowest CH_4 and CO_2 conversion. Stability tests (DRM: 20%CH_4/20%CO_2/He, 100h) performed on the best performing catalysts, namely, 5% Ni/ SBA-15 and 5% Ni/30%CeLa10Cu-SBA-15 catalyst showed a monotonic decrease in coversions rates. Whereas, the conversion rates reached a plateau after approximaitly 40h in the case of the latter catalyst (5% Ni/30%CeLa10Cu-SBA-15).

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Ni-Co bimetallic catalysts for dry reforming of methane: experimental and theoretical approach

Aseel G. S. Hussien[1,2], Aasif A. Dabbawala[1,2], Dalaver H. Anjum[3], Nikolaos D. Charisiou[4], , Balasubramoniam Murali Krishna[3], Marko Gacesa[3], Maria Goula[4], Kyriaki Polychronopoulou

[1,2,*1]*Department of Mechanical Engineering, Khalifa University of Science and Technology, Abu Dhabi 127788, United Arab Emirates*

[2]*Center for Catalysis and Separations, Khalifa University of Science and Technology, Abu Dhabi 127788, United Arab Emirates*

[3]*Department of Physics, Khalifa University of Science and Technology, Main Campus, P.O. Box 127788, Abu Dhabi, United Arab Emirates*

[4]*Department of Chemical Engineering, University of Western Macedonia, Koila, 50100 Kozani, Greece*

[*]*kyriaki.polychrono@ku.ac.ae*

Keywords: Doped ceria, DRM, lattice oxygen, coking, Ni-Co bimetallic catalyst, chitosan, DFT

Introduction: The resurging intrest in dry reforming of methane (DRM: $CH_4+CO_2 \leftrightarrow 2CO+2H_2$) reaction compared to other reforming processes such as steam refirming and partial oxidation is due to the fact that DRM eliminates two main green house gases (CH_4 and CO_2) [1,2]. Consequently, providing an alternative for CO_2 capture, utilization and recycling [3]. Furthermore, the syngas produced is close to unity making it ideal for the Fischer–Tropsch industry [2, 4-5]. However, CH_4 decomposition and CO disproportionation are the main reaction routes of carbon formation during DRM which are the main contributors of catalyst deactivation [4].

Experimental: In this study the optimization of the CeLa10Cu support was performed attempting its synthesis using chitosan and different precipitating agents so to introduce mesoporosity; the CeLa10Cu support with the highest porosity support was used as a carrier of a bimetallic (NiCo) catalyst. Namely, 5 wt.% Ni/CeLa10Cu, 5 wt.% Co/CeLa10Cu, 4.5 wt.% Ni-0.5 wt.% Co/CeLa10Cu, and 2.5 wt.% Ni-2.5 wt.% Co/CeLa10Cu. Alloying of Ni with Co is anticipated to decrease the size of the Ni ensemble and thus to inhibit the formation of carbide and graphite in the reforming reactions. DFT modelling of Ni(111) surface and NiCo(111) surfaces were presented and compared with the experimental results.

Results and discussion: The prepared catalysts were charactarized via a range of techniquies namely XRD, BET, HAADF-STEM, SAED, EELS, elemental mapping, XPS, Raman, CO_2-TPD, H_2-TPR, H_2-TPD. Raman and XRD confirmed the cubic fluorite structure and some heterogeneous phases. Based on the XPS opposite direction peak shifts and HR-TEM images, the formation of NiCo and NiCu bimetallic alloy could be suggested. This could lead to an achieved ensemble size control that ultimately can give rise to decreased carbon formation during DRM. Additional verification of the bimetallic species formation came also from the reducibility profiles of the catalysts. The use of sacrificial template (chitosan) successfully increased the surface area of CeLa10Cu support compared to the same ternary metal oxide support synthesized via EMW reported in [7]. DFT modelling performed on NiCo(111), showed weaker adsorptions for CHx (x=1-4) species, precursors of coke, compared to the Ni(111) surface alone. This is consistent with the reports that weaker C binding suggests a higher surface mobility that lessen carbon deposits over NiCo. Again, the relatively higher CO and O adsorption energies on NiCo (111) compared with Ni(111) surface is expected to facilitate more the DRM reaction while simultaneously decreasing coking. This was also observed in the catalytic studies, where the Ni monometallic (formation of NiCu alloy) and NiCo (4.5 wt. %:0.5 wt.%) bimetallic catalysts supported on CeLa10Cu showed the best catalytic performane towards DRM amongst the other catalysts. The latter catalysts exhibited superior stability over prolonged period of time (DRM: 20%CH_4/20%CO_2/He, 100h) compared to other catalysts.

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Cu-based catalyst deactivation in methanol synthesis by water presence

L. Azancot*, L. Lefferts

Catalytic Processes and Materials, University of Twente, Enschede, The Netherlands
**l.azancot@utwente.nl*

Keywords: CO_2 hydrogenation, Methanol synthesis, catalyst deactivation, $Cu/ZnO/Al_2O_3$ catalysts.

Introduction

The reduction of CO_2 concentration from the atmosphere is the most relevant challenge for society. For this reason, the researchers and industry have highly emphasised in the study of CO_2 reduction, focusing on CO_2 storage and transformation by catalytic processes to liquid fuels or other valuable chemicals. In this way, direct CO_2 hydrogenation to methanol is a promising alternative on a large scale.
The methanol synthesis by CO_2 hydrogenation (Eq. 1) is an exothermic reaction that, based on thermodynamic equilibrium and Le Chatelier's principles the reaction must work at high pressure and low temperature [1].

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H_{298\,K} = -49.5 \text{ kJ mol}^{-1} \quad \text{(Eq. 1)}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H_{298\,K} = 41.2 \text{ kJ mol}^{-1} \quad \text{(Eq. 2)}$$

The water-induced deactivation is an almost unavoidable issue playing a significant drawback in the process, provoking premature catalyst deactivation [2]. The water is produced by the oxygen removal from CO_2, and the reverse Water Gas Shift (rWGS) reaction (Eq. 2) that is thermodynamically favoured under methanol synthesis conditions [3].

The use of Cu-based catalysts for CO_2 hydrogenation is extensive due to is considered a low-cost catalyst. The industrial $Cu/ZnO/Al_2O_3$ catalyst is widely studied for methanol synthesis from syngas or direct CO_2 conversion, nevertheless presents a significant deactivation over time in industrial conditions [4,5]. It is crucial to understand the structural catalyst surface evolution over time and insight into the deactivation causes. An important task that is still under debate that providing different opinions. In this context, this work is focused on the catalyst properties changes during the methanol synthesis reaction using a commercial $Cu/ZnO/Al_2O_3$ catalyst.

Acknowledgments
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Stability promotion of Ni foam catalysts for dry reforming of methane

A. Choya[1*], B. de Rivas[1], J.I. Gutiérrez-Ortiz[1], R. López-Fonseca[1]

[1]*Chemical Engineering Department, Faculty of Science and Technology, University of the Basque Country UPV/EHU, E-48940, Leioa, Spain*

Keywords: dry reforming, nickel, ceramic foams, stability, coke

Introduction

The dry reforming of methane (DRM) reaction is a very promising catalytic process to produce syngas, using greenhouse gases as feedstock, which can then be used to synthesise valuable chemical and fuels [1]. Catalysts derived from the $NiAl_2O_4$ spinel have demonstrated a promising performance for the DRM reaction due to the strong metal-support interaction [2]. Further, the incorporation of this type of materials on a structured support, such as a ceramic foam, can allow for the efficient operation under high space velocities and moderate temperatures. However, the main drawback of this technology is the favoured formation of carbonaceous deposits on the catalyst surface, which strongly affects catalyst durability [3]. Thus, in this work, we study the promotional effect of La_2O_3 over the stability of a $NiAl_2O_4$-mediated nickel catalyst supported over ceramic open cell foams.

Experimental

The foam catalysts were synthesised by solution combustion synthesis. The α-Al_2O_3 foams were submerged for 5 min in a solution of glycine (fuel) and nickel, aluminium and lanthanum nitrates. The concentration of nitrates was adjusted to obtain a stoichiometric $NiAl_2O_4$ phase with a concentration of La in the 0-10%wt. range. Then, the impregnated foams were placed in an oven at 300 °C for 30 min to start the combustion reaction. The impregnation/combustion cycle was repeated 4 more times to deposit a total metallic loading of 10%wt., and then the coated foams were calcined at 850 °C for 4 h. The catalysts were characterised by XRD and H_2-TPR and tested in a bench-scale reactor at 700 °C for 72 h. The reaction feedstream was composed of 10%CH_4/10%CO_2/80%N_2 with a space velocity of 96,000 h^{-1}. Prior to the reaction the calcined foams were subjected to reduction with 5%H_2/N_2 at 850 °C for 4 h.

Results and discussion

The characterisation of the calcined foam catalysts by XRD only detected signals attributable to the ceramic matrix of the foam and a phase of $NiAl_2O_4$. No signals associated with segregated La_2O_3 were observed, which pointed out a good dispersion of this promoter. After reduction, the $NiAl_2O_4$ precursor converted into Ni crystallites with an average size around 10 nm. The analysis by H_2-TPR did not evidence differences in the reducibility of the $NiAl_2O_4$ spinel with the La loading. Also, the quantification of the H_2 uptake evidenced that more than 90% of the deposited Ni was in the form of $NiAl_2O_4$, with very low amounts of segregated NiO. The evolution of CH_4 conversion with time on stream (Figure 1) of the freshly reduced samples evidenced a promotional effect of the added La on the catalyst stability. Hence, the La-free sample suffered a dramatic loss of activity after 60 h, while the La promoted catalysts were able to operate for the whole 72 h interval with a constant conversion of 58-63%. After the reaction runs, direct gravimetry of the unpromoted spent catalyst revealed a coke generation of 1.47 g_C g_{CAT}^{-1} , in line with its drastic deactivation. Conversely, coke formation for the La promoted catalysts ranged between 0.40 g_C g_{CAT}^{-1} for the 6La sample, which exhibited almost no activity loss, and 0.90 g_C g_{CAT}^{-1} over the 10La sample, which suffered a significant conversion loss at the start of the run.

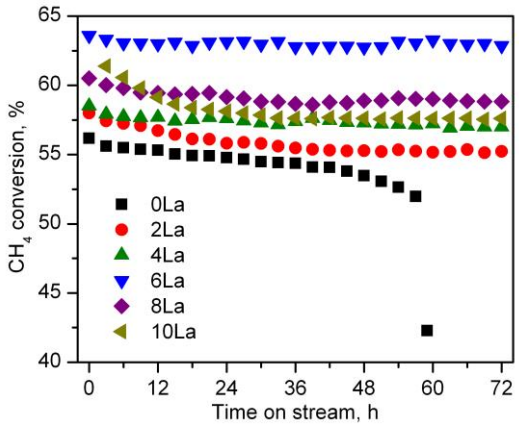

Figure 1. Evolution of CH_4 conversion with time on stream at 700 °C.

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Direct Alcohol Synthesis Over Cu-zeolite Catalysts

D. Iltsiou[1*], J. Mielby[1], S. Kegnæs[1]

[1]*Department of Chemistry - Technical University of Denmark, Lyngby, Denmark*
**dimilt@kemi.dtu.dk*

Keywords: catalysis, zeolites, hydrogenation

Introduction.

As an inexpensive, abundant and non-toxic, renewable carbon source, the use of CO_2 has received a great interest in many areas. Lately, the focus of researchers is the production of fuels and high-value-added chemicals such as alcohols, throughout the hydrogenation of CO_2. Among alcohol products, ethanol attracts great attention due to its notable energy density and current engine knowledge. However, the conversion of CO_2 to ethanol has been difficult, due to the presence on the catalyst of various functional groups and the high energy barrier of the C-C coupling [1]. Therefore, the development of novel stable heterogeneous nanoparticle catalysts, for the selective production of ethanol directly from CO_2, is of great importance. Zeolites are the most widely used industrial heterogeneous catalysts. They are classified as aluminosilicate materials with intracrystalline pores and cavities of molecular dimensions. The catalytically active sites in zeolite micropores can be acid sites that result from the charge compensation of the framework with protons, which is necessary when e.g. Al^{3+} substitutes Si^{4+} in the framework. Alternatively, it can also be redox active sites resulting when the charge compensation is done with redox active ions such as Cu(II), rather than with protons [2].

Experimental/methodology.

Here we report the synthesis and encapsulation of three different zeolite frameworks, with metal nanoparticles, through the interzeolite transformation of FAU [1]. The different zeolite-based catalysts were tested under high pressure continues flow conditions in order to optimize the selectivity for ethanol. We have shown that, the structure of the zeolite framework has great influence on the catalytic activity. All the obtained materials were characterized using IR, XRD, BET, TEM and ss-NMR [1]. Figure 1 shows the different zeolite frameworks used, as well as an illustration of the flow reactor.

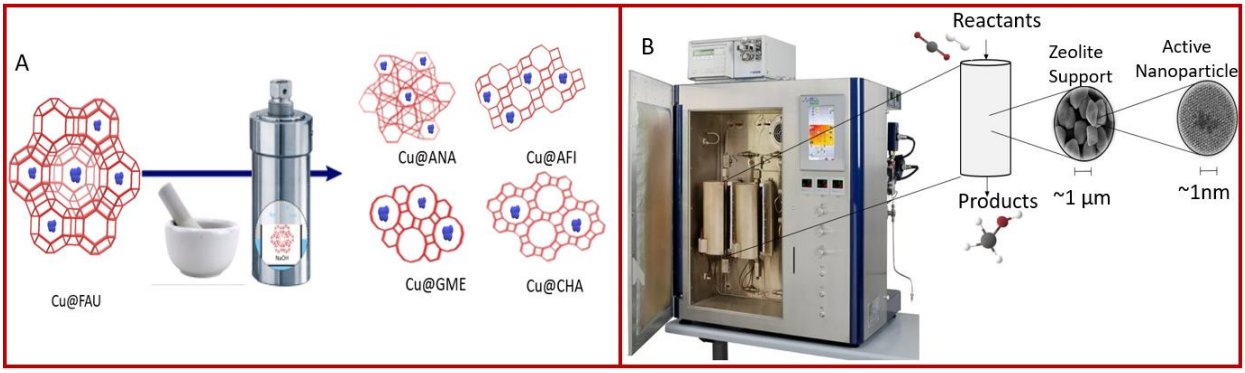

Figure 1. Overview of the zeolite synthesis and the formation of ethanol from CO_2 in a flow reactor.

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Tuning the size of Ni nanoparticles to study structure sensitivity in CO_2 hydrogenation

Bram Kappé[1], Metin Sen[1], Ward van der Stam[1], Esther Groeneveld[2], Matteo Monai[1,*], Bert Weckhuysen[1,*]

[1]*Inorganic Chemistry and Catalysis group, Utrecht University, Utrecht, The Netherlands*

[2]*BASF Nederland B.V., De Meern, The Netherlands*

[*] *m.monai@uu.nl, b.m.weckhuysen@uu.nl*

Keywords: Colloidal Synthesis, Ligand Removal, Operando Spectroscopy, Nickel, CO_2 methanation

Introduction. CO_2 methanation over supported Ni catalysts has recently attracted much attention for energy storage and grid stabilization. Better catalysts with accurate size control are needed since CO_2 methanation was found to be structure sensitive with an optimal activity at 2-3 nm Ni particle size.[1,2] Here, we have employed colloidal synthesis to precisely and independently tune Ni nanoparticle size, catalyst weight loading and support type. We report a colloidal synthesis method using novel phosphine-free ligands capable of yielding Ni NPs sized below 3 nm, which is smaller than reported before in literature.[3] Ligand removal is neccesary to allow surface access during catalysis, but has proven challenging since harsh oxidative treatments can cause the Ni NPs to sinter.[3] Here, we present a chemical method for ligand removal, which does not require heating and maintains the pristine Ni NP size.

Experimental/methodology. Ni NPs were synthesized by injection of a borane tert-butylamine solution into a toluene solution of Ni(acetylacetonate)$_2$ and benzonitrile or mesitylamine as ligand. The Ni NPs were supported on silica and treated with triethyloxonium tetrafluoroborate (Meerwein's reagent, MR) to remove the ligands. Reduction of the Ni/SiO_2 powder at 550 °C, yielded the final catalyst material.

Results and discussion. By optimization of several synthesis parameters, such as reaction temperature, type of ligands, and equivalents of ligands and reducing agents, we obtained Ni nanoparticles in sizes ranging from 1.4–6.6 nm (Figure 1A). To remove the ligands, the Ni/SiO_2 catalysts were treated with MR, which is thought to alkylate the coordinating N moiety of the ligands (Figure 1D), rendering them unable to bind to the Ni surface. DRIFTS was used to follow the ligand removal process. In Figure 1B the vibrational features of the original ligands are shown, while after the treatment these signals are not longer present (Figure 1C, red box). However, large peaks belonging to Si-ethoxy groups are present between 2800–2900 cm^{-1}. By applying a reduction step these ethoxy groups were removed, yielding an active CO_2 hydrogenation catalyst. The catalytic CO_2 hydrogenation activity per Ni surface atom increases by particle size to an apparent plateau (Figure 1E, red; "hockey stick plot"), in contrast to the sharp optimum at ~ 2-3 nm reported in our earlier work for Ni/SiO_2 catalysts (Figure 1E, dark-blue).[1,2] A potential explanation is a decrease in the number of defect sites, which were responsible for the maximum in TOF reported earlier.[4]

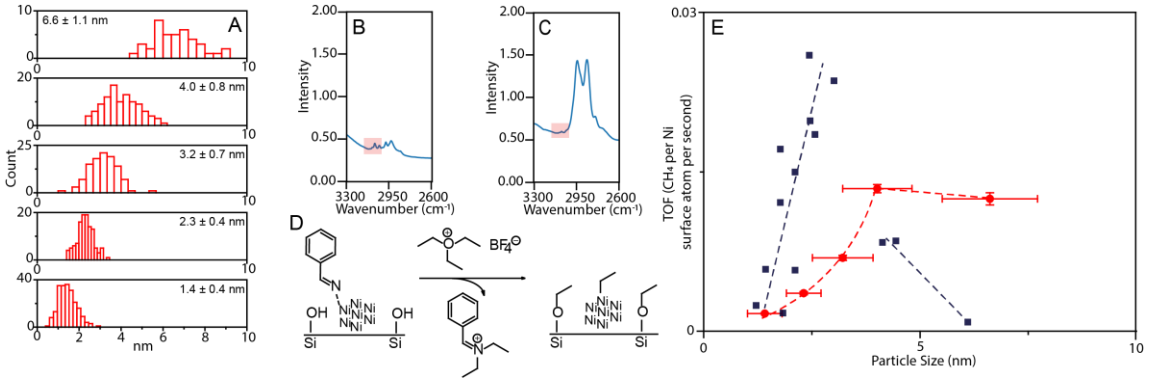

Figure 1: A: Ni nanoparticle diameter distribution based on TEM from various syntheses. B,C: DRIFTS spectrum of Ni/SiO_2 with (B) original ligands or (C) after ligand removal. D: reaction scheme of ligand removal procedure. E: TOF for different mean particle sizes of colloidal-based (this work, red) and deposition-precipitation (dark-blue, previous work) Ni/SiO_2 catalysts in CO_2 hydrogenation towards methane.[1,2] The dotted lines are intended as a guide to the eye.

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The variation of the Zn content on Cu/SiO_2 generates different active sites for the CO_2 hydrogenation to methanol

Daniel Gómez[1], Tomás Vergara[1], Patricia Concepción[2], Romel Jiménez[1], Alejandro Karelovic[1]*

[1]*Carbon and Catalysis Laboratory (CarboCat), Universidad de Concepción, Concepción, Chile*
[2]*Instituto de Tecnología Química, Universitat Politècnica de València, Valencia, Spain*
*akarelov@udec.cl

Keywords: methanol synthesis, copper, zinc, active site, SSITKA

Introduction. Copper-based catalysts are widely studied for CO_2 hydrogenation to methanol, especially Cu/ZnO catalysts which have received attention due to their commercial relevance in the syngas to methanol process. Different active site configurations have been proposed, such as: (i) Cu^+ sites on ZnO, (ii) Cu^0 sites on ZnO (interface) and (iii) CuZn alloy [1,2]. Despite the many studies that have been carried out on Cu/ZnO catalysts, there are still some scientific questions that have not been answered, such as the effect of Zn content on the nature of the active sites and the mechanism. Here we study the role of ZnO on the Cu surface and how the nature of these sites varies as the Zn concentration varies.

Experimental/methodology. Silica-supported Cu and Cu/Zn catalysts were prepared by incipient wetness impregnation method. They were characterized by ICP-OES, HR-TEM, *in situ* XRD, N_2O-titration, IR-CO titration (low temperature), H_2/D_2 isotopic exchange and *quasi-in situ* XPS (before and after reaction). The CO_2 hydrogenation was carried out in a fixed bed reactor at 220-280°C, 8 bar, H_2/CO_2=3 and 1.67 $cm^3\ g_{cat}^{-1}s^{-1}$. SSITKA-DRIFTS experiments were performed in a low volume *in situ* cell at 220°C, H_2/CO_2=7, 3 bar and 6.3-12.5 $cm^3\ g_{cat}^{-1}s^{-1}$.

Results and discussion. CO adsorption shows that Cu/SiO_2 catalyst present a mainly metallic Cu surface after reduction, while the CuZn(0.01) catalyst presented a variety of surface sites, mainly composed of Cu^0, Cu^+ and CuZn alloy. However, CuZn(0.20) presented only Cu^0 and Cu^+ type sites, indicating that these Zn loads do not favor the formation of CuZn alloy type sites (Fig. 1a). In addition, a correspondence was found in the behavior of TOF to methanol with the superficial molar ratio Zn/(Cu+Zn), while TOF_{CO} was adjusted to the Cu content on the surface (Fig. 1b). Zn was found to further promote restructuring of the metallic copper surface when exposed to highly reducing conditions. The SSITKA-DRIFTS experiments revealed, for CuZn(0.01), the formation of highly active sites for CO (Fig. 1c), while for methanol it is only favored by an increase in the number of sites. However, on the CuZn(0.20) catalyst, a 50% reduction of the CO sites was found and an increase of up to almost double the number of methanol sites with respect to the non-promoted catalyst (Fig. 1c), which corresponds to the transformation of active sites to CO on active sites of methanol. In addition, in this catalyst, formate species were identified that proved to be reactive intermediates in the reaction. According to the different chemical states of the surface and the characteristic active sites of each catalyst, a reaction mechanism was proposed that includes the possible reaction pathways that Zn-promoted Cu catalysts can follow.

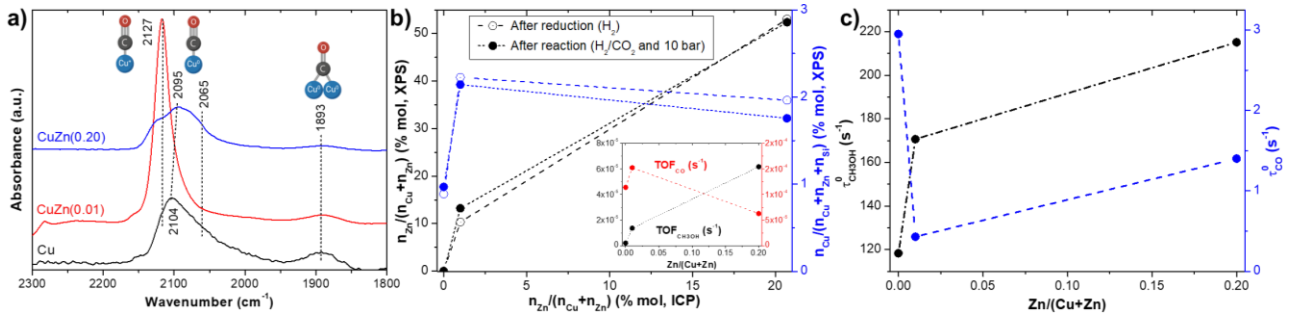

Figure 1. (a) IR spectra of CO adsorption at -160 °C. (b) Surface quantification by XPS: after reduction (empty symbols) and after reaction at 10 bar (full symbols). Small graph its relationship with the methanol and CO formation. (c) Corrected residence time of methanol and CO intermediates as a function of Zn content, determined by SSITKA.

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Mixed metal oxide and zeolite catalysts for carbon dioxide conversion to olefins: A small pore zeolite exploration

Ahmed Sajid[1], Julien Devos[1], Cedric Aelbers[1], Ibrahim Khalil[1], Michiel Dusselier[1*]

[1]*Center for Sustainable Catalysis and Engineering, Celestijnenlaan 200F, KU Leuven, 3000 Leuven, Belgium*
[*]*Michiel.dusselier@kuleuven.be*

Keywords: CO_2 hydrogenation, small pore zeolites, olefins, methanol

Introduction: Combining mixed metal oxides and zeolite catalysts is well known for CO_2 conversion to olefins (CTO) via methanol [1,2]. The process occurs via 2 steps in which the difference in the optimum operating temperatures is significant. The hydrogenation of CO_2 to methanol occurs on the metal oxides typically at 250-300 °C, while the further conversion of methanol into olefins (MTO) takes place over the zeolites, usually at $T \geq 375$ °C [2]. Thus, to improve the efficiency of CTO, the temperature gap must be reduced either by developing new metal oxides with higher operating temperatures (Zn, Zr, Ga, In, Cr), while keeping selectivity for CO minimal; or zeolites with high MTO performance at lower temperatures [1]. In this work, we investigated self-made small pore zeolites [3] in combination with an optimised $ZnZrO_x$ catalyst for CO_2 conversion to olefins. Next to the effect of lattice type, the effect of phyisicochemical zeolite properties such as Al content, acidity, Al speciation, and cation content will be investigated.
Experimental/methodology: $ZnZrO_x$ was synthesized by co-precipitation method, using $ZrO(NO_3)_2$ and $Zn(NO_3)_2$ precursors, while interzeolite conversion was utilized for zeolite synthesis. Physico-chemical properties of the catalysts (acidity) as well CO_2 and H_2 adsorption capacity by TPD were measured. Crystallinity and surface area of the $ZnZrO_x$ and zeolites were detremined by using X-ray diffraction and N_2 physisorption. The activity of the granular-mixed metal oxide and zeolite catalyst was measured in continuous reactor at P = 40 bar, T = 340-380 °C, GHSV = 18000 $ml.g_{cat}^{-1}.h^{-1}$, H_2/CO_2 ratio of 3.
Results and discussion: Figure 1 demonstrates high space time yield (STY) for products derived via MeOH ($STY_{MeOH + DME + olefins + paraffins}$). In comparison, MeOH production for the bare $ZnZrO_X$ only mounts to 11 mol_{MeOH} $kg_{cat}^{-1}.h^{-1}$ (@ 360°C). This demonstating that the equillibrium is shifted towards the product side, despite the dilution of metal oxide catalyst by zeolites (2 oxide/1 zeolite). For the family of CHA (SSZ-13) zeolites, partial cation exchange (Mg^{2+}) slightly improved propylene selectivity, while AEI frameworks (SSZ-39 and SAPO-18) showed great potential. A structure-performance map for different zeolites will be shown.

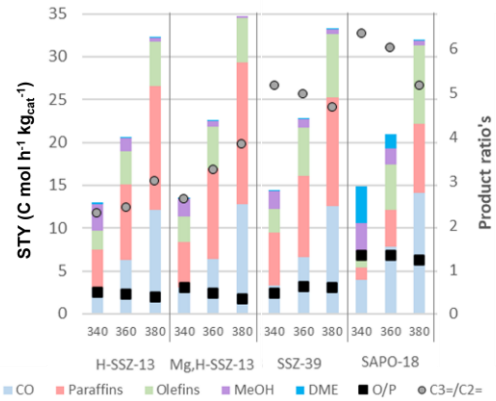

Figure 1: Activity (STY, per gram catalyst) and product distribution of ZnZrOx in tandem with different zeolites.

Acknowledgments
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MOF-derived Fe-Co bimetal catalysts for CO_2 hydrogenation to hydrocarbons

Byeong Gi Kim[1], Jong Wook Bae[*]

[1]*School of Chemical Engineering, SungKyunKwan University (SKKU), 2066 Seobu-ro, Suwon, Gyeonggi-do, 16419, Republic of Korea*
[*]*finejw@skku.edu*

Keywords: Metal-Organic Frameworks(MOFs), CO_2 hydrogenation, Fischer-Tropsch synthesis(FTS)

Introduction.

Productions of fuel-grade hydrocarbons by CO_2 hydrogenation and CO hydrogenation included in syngas are very interesting topics for carbon capture and utilization (CCU). There are two possible routes for CO_2 hydrogenation reaction by using cobalt-based catalysts. One method is the formate pathway where main active sites are metal oxides which mainly produce methane [**1**]. By using the cobalt-based catalysts, CO_2 methanation reaction is also followed by formate pathway. The other route is reverse water-gas shift (RWGS) reaction route where the main active sites are metallic phases, which forms CO to successively be utilized for Fischer-Tropsch synthesis (FTS) reaction. By using the iron and cobalt-based bimetal catalysts, hydrocarbons are synthesized by CO_2 hydrogenation reaction through the second reaction pathway. Iron-cobalt bimetal catalysts can be prepared by using metal-organic frameworks (MOFs) as well. Since the metallic cobalt nanoparticles have a lot of advantages such as higher RWGS activity and higher CO_2 hydrogenation to light hydrocarbons, the adjustment of long chain hydrocarbons (C_2 - C_4 and C_{5+}) can be controlled by introducing iron metal precursors during the MOF-derived catalysts preparation.

Experimental/methodology.

Iron nitrate nonahydrate, cobalt nitrate hexahydrate and terephthalic acid were well mixed at the ratio of x:1:2 in the solution, which was mixed with N,N-Dimethylformamide (DMF) and triethyl amine (TEA). (where x = 5, 3, 2, 1) After stirring and filtering, the successive washing step was performed with DMF and dried at 40 °C. As-prepared brown color powders were obtained and its was denoted as Fe_xCo_1-BDC. For pyrolysis step, well-made catalysts was pretreated at 600 – 900 °C on N_2 atmosphere. And its was named as P_y-FeCo – BDC (y = pyrolysis temperature, 600 – 900 °C)

Results and discussion.

Catalytic performances of each catalyst were displayed in **Figure 1.** Different activities were observed in terms of CO_2 conversion, CO selectivity, and hydrocarbons selectivity as well. Increased conversion and decreased CO selectivity were attributed to the cobalt metal contribution as well as increased hydrocarbons and decreased methane selectivity were mainly attributed to the iron carbides phases.

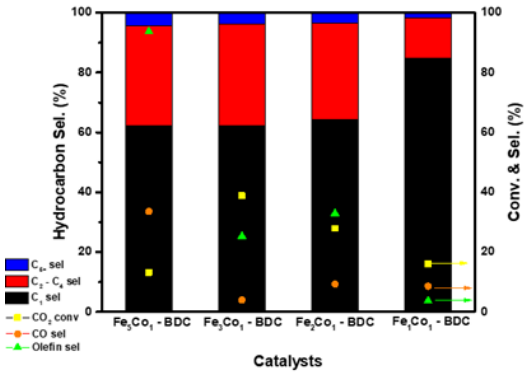

Fig. 1. Catalytic activity of Fe_xCo_1 – BDC (x = 5, 3, 2, 1 for molar ratio between iron metal and cobalt metal precursor)

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Effect of carbonate content on the rheological properties of poly(propylene carbonate) polyols

Harin Kim, Jiwon Hwang, Su Min Jung, Hyo-Jeong Lee, Jun Dong Park, Joon Hyun Baik*

Department of Chemical & Biological Engineering, Sookmyung Women's University, Seoul, Republic of Korea
**joonhyun@sookmyung.ac.kr*

Keywords: Double metal cyanide complex catalyst, CO_2 chemical utilization, CO_2 Polyol, Rheology

Introduction

Carbon dioxide (CO_2) is being generated from many industrial operations, and it is recognized as the major component for global warming. Therefore, Carbon Capture and Utilization (CCU) technology is being offered as a solution to this problem. An interesting strategy appears to be the direct chemical use of CO_2 as a co-monomer in polymerization reactions to produce value-added materials [1]. Polyols, which have two or more hydroxyl groups per molecule, are the major raw material for polyurethane foams (PUFs) [2]. The catalytic copolymerization reaction of propylene oxide (PO) and CO_2 produces polycarbonate (PC) polyol or poly(propylene) carbonate (PPC) polyol depending on the catalysts [1]. The PC polyol is difficult to employ to prepare flexible PUFs due to its technical limitations such as high glass transition temperatures (T_g) and high viscosity at ambient temperature [1,3]. On the other hand, PPC polyol can be produced over the Double Metal Cyanide (DMC) catalysts, which has a favorable T_g and low viscosity [4]. Thus, we investigated the effect of carbonate content on the rheological behavior of CO_2-based polyol to find affordable content for manufacturing flexible PUFs.

Experimental/methodology

DMC catalysts were prepared with $ZnCl_2$ as a metal salt and $K_3[Co(CN)_6]$ as a metal cyanide salt in the presence of P123 as a complexing agent. Copolymerization of PO with CO_2 was carried out in a 450 mL high-pressure reactor at 115 °C. PPG-1000 was used as an initiator for copolymerization. The reactor pressure maintained by using CO_2 from 5 to 25 barg. After purifying the polyols to remove cyclic propylene carbonate (cPC), the rheological properties with respect to the carbonate contents were analyzed.

Results and discussion

The calcination temperature of the DMC catalyst was optimized to increase catalytic activity. Among them, DMC-P123 catalyst calcined at 100 °C showed the highest productivity and the shortest induction period mainly due to the formation of monoclinic structure of the catalyst. The carbonate contents (F_{CO2}) in the polyols over this catalyst were controlled by altering the reactor pressure (Fig. 1a). The viscosity of PPC polyols tended to increase along with their carbonate content (Fig. 1b). This result demonstrates that the carbonate groups in the polyols create greater interaction between them and provides crucial information on choosing CO_2-based polyols for flexible PUFs.

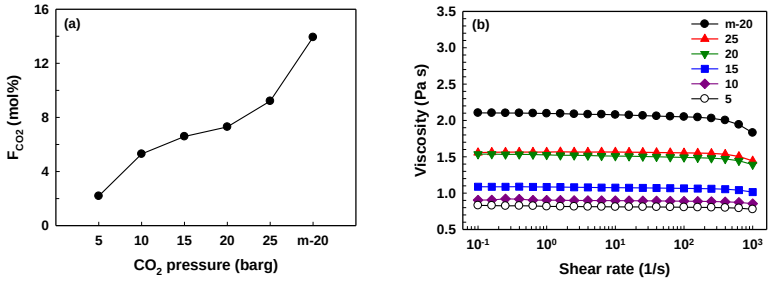

Fig. 1. Effect of reactor (CO_2) pressure on (a) CO_2 mole fraction and (b) viscosity vs. shear rate flow curves of PPC polyols.

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Assessing the influence of high pressure on the electrochemical reduction of CO_2 using atomic-scale spacing over SnO_x nanoparticles

Sheraz Ahmed[1], Muhammad Kashif Khan[2,3], Jaehoon Kim[1,2,3*]

[1]*SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon, South Korea*
[2]*School of Chemical Engineering, Sungkyunkwan University, Suwon, South Korea*
[3]*School of Mechanical Engineering, Sungkyunkwan University, Suwon, South Korea*
[*]*Jaehoonkim@skku.edu*

Keywords: High Pressure, CO_2 reduction, Acetone, Interparticle spacing

Introduction: The anthropogenic CO_2 emission can be mitigated by developing electrochemical reduction of CO_2 (CO_2RR) to value-added chemicals and fuels [1]. Several heterogeneous metal and metal oxides-based catalysts have been developed for CO_2RR, but it is still a great challenge to improve the current density and Faradaic efficiency (FE) of the single product. In typical aqueous CO_2RR, the FE is limited due to the competitive hydrogen evolution reactions (HER). The electrocatalytic performance is improved by increasing supply of CO_2 to the cathode compartment. The hydrated CO_2 (aq) and H_2CO_3 species play a crucial role in CO_2RR according to Henry's law. Typically, Sn-based metal oxides at high pressures reveal the selective production of formate/formic acid, an important chemical for large-scale industrial products and processes [2]. The extensive investigation reveals that the exposure of atomic-scale spacing has been demonstrated as an effective approach toward the enhancement of kinetics and mass transport, which results in enhanced product selectivity towards acetone.

Experimental/methodology: The LiET(S) SnO_x catalyst was synthesized by the lithiation process, and the structure can be controlled by the galvanostatic discharge voltage which varies with the extent of Li insertion.

Results and discussion: A 3D STEM tomography is the technique to determine the precise structure of a sample in atomic-scale resolution. Fig. 1, shows the series of STEM images at certain titled angles and tomographic images. A clear and smooth surface of pristine SnO_2 was observed without any significant changes in the structure as seen TEM image and STEM tomography. Furthermore, the formation of disintegrations/defects was confirmed by the TEM and STEM tomography analyses. The application of non-noble Sn-based nanoparticles was synthesized by generating grain boundaries with controlled sub-nanoscale-sized spaces. It has been a great challene to convert CO_2 to C_{2+} products using Sn-based catalysts because of the high CO_2 activation barrier and C-C coupling. The combination of the confinement effect and high pressure on LiET(S) SnO_x, reveals the selective production of acetone (FE ~ 55 %) at high pressure of 100 bar at industrially relevant conditions.

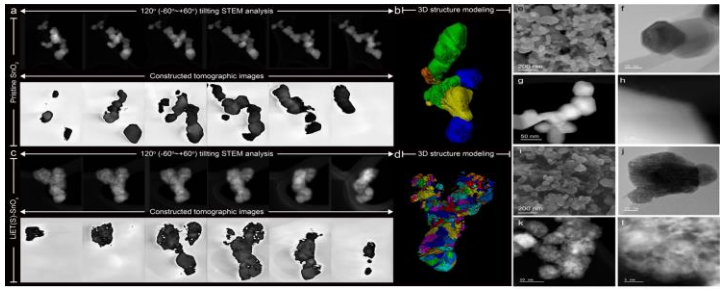

Fig: 1. (a and c) STEM images along 120˚ rotating from -60 to +60˚, 3D STEM-tomography and (b and d) reconstructed 3D structure modeling images of pristine SnO_2 and LiET(S) SnO_x, (e to h) SEM and TEM images of pristine SnO_2 while (i-l) SEM and TEM images of LiET(S) SnO_x.

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Effect of La_2O_3 and CeO_2 Promotion on CO_2 Conversion to Methane Using Mesoporous ZSM-5, US-Y and BEA Supported Ni-Catalysts

A. Kızıl[1], B. Ipek[1*]
[1]*Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey*
[*]*bipek@metu.edu.tr*

Keywords: CO_2 Methanation, Zeolites, Nickel

Introduction. CO_2 methanation is a promising process that can reduce CO_2 emissions. Nickel-based catalysts are economical catalysts; however, Nickel particle size is inversely related to catalytic activity [1], [2]. Zeolites are appropriate supports for CO_2 methanation because of their thermal and hydrothermal stability, hydrophilic or hydrophobic characteristics depending on the Si/Al ratio and CO_2 adsorption ability due to compensating cations. In addition, they have modifiable pore structure via formation of mesopores, which can potentially prevent sintering of reduced Nickel particles [3]. La_2O_3 and CeO_2 promotions are reported to improve the surface properties of Nickel-based catalysts, enhancing methanation activity [4]. This study aims to develop mesopores in three different zeolite frameworks, FAU, BEA and MFI, with similar Si/Al ratios to understand the effect of Na^+ and Cs^+ as compensating cations and La_2O_3 and CeO_2 as promoters on the CO_2 methanation.

Experimental/methodology. ZSM-5 was synthesized by hydrothermal method. Consecutive dealumination and desilication were applied using steaming and NaOH treatment to increase the mesopore volume. Beta was obtained commercially. Mesopores on commerical Beta (Thermo Fisher, Si/Al=19) were formed by dealumination using 0.065 M HNO_3 solution. Mesopore added US-Y was obtained commercially (Thermo Fisher, Si/Al=40). All samples were ion-exchanged by Na^+ and Cs^+ using $NaNO_3$ and $CsNO_3$. Nickel and La_2O_3 and CeO_2 promoters were added using incipient wetness impregnation method. Crystal structure, chemical composition, physico-chemical properties, surface basicity, H_2 consumption rates and morphology were analyzed by XRD, ICP-OES, N_2 Physisorption, CO_2-TPD, H_2-TPR and SEM, respectively. The catalytic activity tests were performed in a fixed bed reactor at atmospheric pressure under the flow of H_2:CO_2 with a 4:1 molar ratio at a constant GHSV of 12500 h^{-1} at 300, 350 and 400 °C.

Results and discussion. US-Y, BEA and ZSM-5 having similar Si/Al ratio of 40 with 10 wt% Ni and 2.5 wt% La_2O_3 or CeO_2, had mesopores after dealumination/desilication, resulting in Ni^0 particle sizes of the order of 10 nm. La_2O_3 enhanced the total basicity and CeO_2 improved Ni^0 dispersion by decreasing the Ni^0 particle size, both showing improved CO_2 methanation activity. US-Y and BEA exchanged with Cs^+ and Na^+ showed similar CO_2 methanation activity; however, Cs^+-exchanged ZSM-5 showed very low activity, which may be attributed to 18 nm of Ni^0 particle size and pore blockage by Cs^+ ions. At 300 °C, Ni-CeO_2/Na^+-BEA catalyst exhibited the highest CO_2 conversion of 83% with 99% CH_4 selectivity, having Ni^0 particle size of 8 nm. Ni-CeO_2/Na^+-BEA catalyst was stable for 30 h at 300 °C, and resistant to sintering.

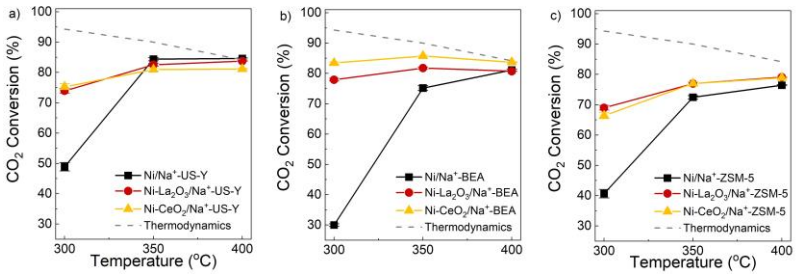

Figure 1. CO_2 Methanation Activity of Na^+-Exchanged Zeolites a) US-Y, b) BEA, c) ZSM-5

Acknowledgments. *This project is funded by TÜBİTAK with Project number: 122M396.*

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One step CO_2-to-Dimethyl Ether Conversion over Bi-functional 3D-printed ZSM-5-based Catalysts

V. Koidi[1,2*], S. Koltsakidis[1], E. Tzimtzimis[1], D. Tzetzis[1], A.A. Lappas[2], E. Heracleous[1,2]

[1]*School of Science and Technology, International Hellenic University, 57001 Thessaloniki, Greece*
[2]*Chemical Process & Energy Resources Institute (CPERI), Centre for Research and Technology Hellas (CERTH), 57001 Thessaloniki, Greece*
[*] *v.koidi@ihu.edu.gr*

Keywords: Dimethyl Ether (DME), CO_2 hydrogenation, 3D printing, bifunctional catalysts, ZSM-5

Introduction. One-step Dimethyl Ether (DME) synthesis from CO_2 presents an attractive approach for CO_2 emissions reduction through its valorization. Thermodynamically, the catalytic hydrogenation of CO_2 to DME is favorable. However, the one-step process poses significant challenges, as it requires the use of suitable bifunctional catalysts, containing both metallic and acidic active sites for simultaneous CO_2 hydrogenation and methanol dehydration respectively at the same reaction conditions. Even though catalyst design via 3D printing is still in infancy, it can prove extremely useful for the customized fabrication of structured materials with improved catalytic performance and transfer phenomena. In this study, we explore the use of additive manufacturing to develop Cu-ZSM-5-based catalysts for the one-step CO_2 hydrogenation to DME.

Experimental/methodology. ZSM-5 based monoliths (3D40, 3D50, 3D60) were prepared via the Direct Ink Writing method, using pastes with different concentrations of bentonite binder and ZSM-5 zeolite, selected due to its high acidity [1]. The materials were first screened in the methanol dehydration to DME reaction. The optimum catalyst was then impregnated with different Cu/Zn content and calcined at 350 °C for 6 h in air. The catalysts were characterized to determine their textural properties (BET), crystallinity (XRD), acidity (FT-IR pyridine) and metal content (ICP-AES). The catalytic performance was assessed in a continuous high-pressure dual fixed-bed reactor unit. A mechanical mixture of commericial ZSM-5 and $Cu/ZnO/Al_2O_3$ catalysts in powder form was also used as reference in a mass ratio 1:1.

Results and discussion. Characterization of the 3D printed monoliths revealed that the ZSM-5 crystals retain their physicochemical characteristics and are not significantly affected by the 3D printing process. Increasing the ZSM-5 content in the monoliths led to better activity results in the methanol dehydration reaction, which is related to the increased acidity. All catalysts achieved 100% DME selectivity under the investigated conditions.

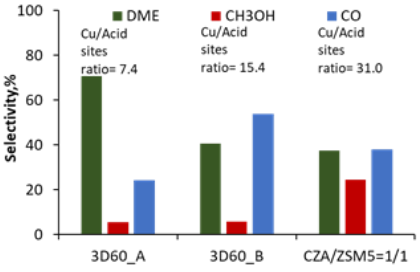

Figure 1 Product selectivities over Cu-ZSM-5-based catalysts (T=250 °C, P=70 bar, H_2:CO_2=3, W/F=0.3g.s/cm^3)

The optimum ZSM-5 based monolith (3D60) was impregnated with Cu/Zn at a weight ratio of 1.5 with different total loading (3D60_A: 8.5 wt. %, Cu, 5.7 wt.% Zn | 3D60_B: 15.2 wt. % Cu, 10.4 wt. % Zn). Impregnation led to additional diffractions in the XRD diffractograms characteristic of CuO and ZnO, whose intensity increases with higher metal content. The metals also affected significantly the acidity, by completely blocking the Brønsted acid sites, but increasing the total acidity by generating new acid sites of Lewis nature. Testing in the one-step CO_2 hydrogenation reaction (T=250 °C, P=70 bar, CO_2:H_2=3) revealed a correlation between the Cu/acid sites ratio and the product distribution and activity, highlighting the prospects of 3D printing in catalytic applications.

Acknowledgments
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Promoted Ni/Zeolite catalysts for thermal and DBD plasma-assisted CO_2 methanation: On the role of the promoter nature

Golshid Hasrack[1,2], Carmen Bacariza [2,*], Carlos Henriques[2], Patrick Da Costa[1]

[1]*Institut Jean Le Rond d'Alembert, Sorbonne Université, CNRS UMR 7190, Saint-Cyr-l'Ecole, France*
[2]*Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1049 001 Lisboa, Portugal*
[*]*maria.rey@tecnico.ulisboa.pt*

Keywords: Plasma-catalytic methanation, Nickel, Ceria, Zeolite, promoters.

Introduction. Carbon dioxide hydrogenation into synthetic fuels and value-added chemicals constitutes a suitable strategy to stabilize anthropogenic greenhouse gas emissions. Methanation or Sabatier reaction is one of the potential pathways to valorise CO_2, being the use of catalysts required. Ni-based catalytic systems have been the most widely explored [1] while, in the last years, plasma-assisted methanation has revealed promising results and is reaching nowadays an industrialisation process [2]. However, catalysts' design is still under debate, being multiple supports reported. In this way, improving catalysts' formulation to boost plasma catalysis synergies towards CO_2 methanation is key [3]. In the present work, thermal and non-thermal plasma (NTP)-assisted CO_2 methanation were performed over promoted Ni-based zeolites with the aim of identifying the promotion effect on their chemical and physical properties and their performances for methane production.

Experimental/methodology. Zeolite-based catalysts containing 10 wt% of Ni and variable loadings of promoters (e.g., Ce, Co, La) were prepared by wet impregnation followed by calcination at 500 °C. For this purpose, a commercial HUSY zeolite (Si/Al=38) was used as support. Samples were characterized by powder X-ray diffraction (XRD), N_2 sorption, temperature programmed reduction with H_2 (H_2-TPR), temperature programmed desorption of CO_2 (CO_2-TPD) and transmission electron microscopy (TEM). Thermal CO_2 methanation tests were conducted from 200 to 500 °C in a tubular fixed-bed glass U-type reactor at 1 atm. Plasma catalytic tests were performed in a DBD plasma reactor after a cleaning step under H_2 flow for 10 min at 12.3 kHz and 21 kV. In the plasma-catalytic hybrid process, the energy was supplied by a high voltage 30 kHz (MiniPuls 6) and voltages applied ranged from 21 to 29 kV (peak to peak). The applied voltage was measured by a digital picoscope with a probe. The same gas hourly space velocity (GHSV) was kept in all tests, to allow a proper comparison with the results from the thermal experiments. In both cases, metal-containing catalysts were pre-reduced at 500°C for 1 h under a flow of 5%H_2/Ar.

Results and discussion. The incorporation of cerium over Ni/Zeolite by an optimized wet impregnation strategy led to an improvement of the thermal and NTP catalytic activity towards CO_2 methanation. Indeed, a CH_4 yield increase from 4 to 28% at 350 °C was registered under thermal conditions for Ni/Zeolite and NiCe/Zeolite, respectively. In the case of plasma catalysis, Ce addition led to an increase of the CH_4 yield from 15 to 40% at 14.5 kV. This beneficial effect was attributed to the enhanced of CO_2 activation and Ni^0 dispersion after Ce incorporation. Furthermore, doping this optimized NiCe/Zeolite system with additional promoters such as Co or La did not lead to a systematic improvement of the catalytic performances. Indeed, among the tested promoters, Co was the one leading to highest improvement of the CO_2 conversion and CH_4 selectivity both under thermal and NTP catalytic conditions. This effect was again ascribed to the reduction of the average Ni^0 crystallite size and the improvement of the number of basic sites after cobalt addition.

Acknowledgments

This work was carried out in the framework of Plasma Catalysis CO_2 Recycling (PIONEER) project which has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 813393. Authors thank also Fundação para a Ciência e Tecnologia (FCT) for CQE funding (UIDB/00100/2020 and UIDP/00100/2020) and Carmen Bacariza' contract (2020.00030.CEECIND).

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Supported catalysts for the Reverse Water-Gas Shift reaction

E. Kowalewski[1], M. Kock[1], S. Viðarsson[1], J. Mielby[1], S. Kegnæs[1]*

[1]*Technical University of Denmark, Kgs. Lyngby, 2800, Denmark*
[*]*skk@kemi.dtu.dk*

Keywords: CO_2, hydrogenation, Reverse Water-Gas Shift reaction, RWGS

Introduction. Constant and not fully controlled development has led modern civilization to a breakthrough point in which further operating on the current principles may lead to a climate catastrophe. The CO_2 concentration in the atmosphere has reached an alarming level and the detrimental effects are already visible [1]. Fortunately, the solution to this vital problem could bring more benefits than a clean atmosphere. Catalytic hydrogenation of CO_2 via Reverse Water-Gas Shift reaction (RWGS) can be an excellent source of syngas used for sustainable production. Countless catalysts have been tested for this reaction all around the world [2]. Nevertheless, there is still a strong need to search for better and more economically balanced catalysts. In the presented work we demonstrate the catalytic behavior of not previously tested Manganese based catalysts and show the influence of various support materials and the promoting effect of alkali metals on their performance in Reverse Water-Gas Shift reaction.

Experimental/methodology. All catalysts have been tested under atmospheric pressure in a flow reactor equipped with a NDIR detector, tuned for CH_4, CO and CO_2. Catalytic experiments were performed at a range of temperatures with additional high temperature stability test (1 atm, H_2:CO_2 ratio - 3:1). Selected samples were subjected to operando IR studies in Nicolet iS50 FTIR spectrometer equipped with a Harrick Praying Mantis Cell with an on-line mass spectrometer by Pfieffer Vacuum OmniStar. Catalysts' structural and physicochemical properties were determined by N_2 physisorption, TPR, XRD, XPS, SEM and TEM measurements.

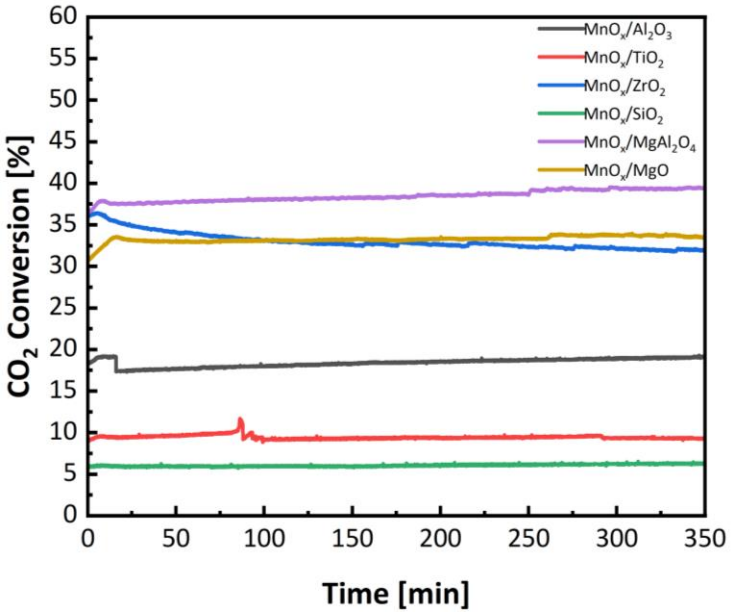

Figure 1. Catalytic hydrogenation of CO_2 with Manganese supported catalysts (1 atm, H_2:CO_2 - 3:1).

Results and discussion. Manganese based catalysts demonstrated entirely different catalytic performance depending on the used support materials (Figure 1) [3]. The observed differences are related to the physicochemical properties of the catalysts, e.g. the presence of oxygen vacancies, basic and acidic sites. Furthermore, we observed the beneficial effect of the addition of alkali metals on the catalytic performance of such catalytic systems. Additional operando measurements revealed intermediate species in the CO_2 hydrogenation on Manganese catalysts, which allowed us to draw some conclusions regarding the reaction mechanism.

Acknowledgments

This work was supported by the Independent Research Fund Denmark under the Green Transition Program.

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Fe-Zr catalysts for direct synthesis of light olefins via CO_2 hydrogenation

E. Kraleva[1*], U. Armbruster[1], S. Wohlrab[1]

[1]*Leibniz Institut for Catalysis, Rostock, Germany*
elka.kraleva@catalysis.de

Keywords: carbon dioxide; hydrogenation; light olefins; iron-zirconium catalysts

Introduction

The demand for light olefins C_2-C_4 as raw materials for the production of chemicals (e.g. plastics and fibres) increases worldwide every year. Recently, there has been a growing interest to produce light olefins in an innovative sustainable way from CO_2 and green H_2 as feedstock. The main challenge is the development of effective catalysts for this CO_2 hydrogenation, which implies high CO_2 conversion, high C_2-C_4 selectivity, high olefin/paraffin ratio and low CO and CH_4 selectivity [1-2].

Experimental/methodology

Fe-Zr metal oxide catalysts with La and K addition were prepared by impregnation and via citrate combustion. After calcination, the structural features were studied by XRD, N_2 physisorption, XPS, TPR-H_2. The catalysts (200 mg, 0.2-0.4 mm) were tested in CO_2 hydrogenation at isothermal conditions in a single-channel set-up. A layer of SiC (800 mg, SiC, 0.3-0.5 mm) was added on top of the catalyst bed to preheat the feed and to ensure plug flow. Feed and product gas were analyzed by on-line gas chromatograph (FID + TCD). Before testing, the as-prepared catalysts were heated to 400 °C and reduced in H_2 for 4 h (1.0 bar). Then, the catalysts were evaluated in CO_2 hydrogenation ($CO_2/H_2/N_2$ = 1:3:1; 30 bar; 300, 350 and 400 °C; GHSV = 6000 $ml \cdot h^{-1} \cdot g^{-1}$; each condition 10 - 24 h).

Results and discussion

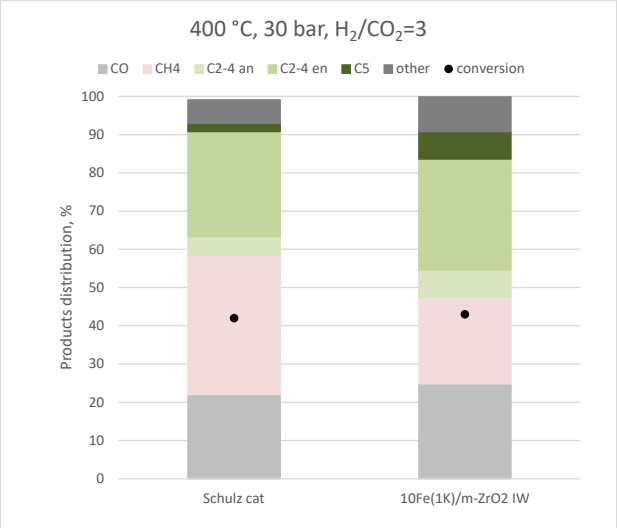

Figure 1. Catalytic activity of the samples for CO_2 hydrogenation. Comparison between benchmark catalyst (Schulz cat) and our 10Fe(1K)/m-ZrO_2 IW sample under the same reaction conditions.

Our research focuses on the effect of different ZrO_2 carriers on the evolution of active Fe phases for CO_2 conversion to light olefins. Moreover, we investigate the effect of promoters, like La or K, on the properties of Fe-Zr-K catalysts to regulate the product distributions and to enhance the yield of desired light olefins. By means of *in situ* characterization techniques (XRD, XPS, and TPR) we also investigated the synergetic effect between La and Zr on the dynamic evolution of iron and surface carbon species. Thus, a structure-activity relationship between the dynamic evolution of active species and the rate of CO_2 hydrogenation to light olefins is proposed. At a Fe loading of 10 wt %, the catalyst 10Fe(1K)(1La)/m-ZrO_2 showed remarkable CO_2 conversion (42%) and high selectivity and stability to light olefins (32%). The Fe(K)/m-ZrO_2 sample demonstrated better product distribution under the same reaction conditions compared to a benchmark catalyst from literature (FeCuAlK) [3], with lower methane formation and high olefin selectivity (Figure 1).

Acknowledgments

Funding by BMWi (FKZ 03EE5060B) is gratefully acknowledged

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Controlling Ethylene Selectivity in Direct CO_2 Hydrogenation

Y. Kuddusi[1,2*], L. Piveteau[3], A. Züttel[1,2]

[1]*Laboratory of Materials for Renewable Energy (LMER), Institute of Chemical Sciences and Engineering, Basic Science Faculty (SB), École Polytechnique Fedérale de Lausanne (EPFL), 1950 Sion, Switzerland*
[2]*Empa Materials Science & Technology, 8600, Dübendorf, Switzerland*
[3]*Institute of Chemical Sciences and Engineering, École Polytechnique Fedérale de Lausanne (EPFL), 1015 Lausanne, Switzerland*
[*]*yasemen.kuddusi@epfl.ch*

Keywords: CO_2 hydrogenation, ethylene, light olefins, gallium oxide, bifunctional catalyst

Introduction

Nature possesses many carbon cycles in which energy is stored[1]. Likewise, thermo-catalytic hydrogenation of carbon dioxide enables energy to be converted and stored in the chemical bonds of produced hydrocarbons. Current production of high-value chemicals such as ethylene and propylene is based on fossil feedstocks and emit at least 0.81 $tons_{CO2}$ per ton of the produced chemical[2]. Carbon dioxide when used as a carbon feedstock along with hydrogen retrieved from renewable resources offers an alternative green pathway for the synthesis of these hydrocarbons.

Direct CO_2 hydrogenation to olefins follows either a methanol-mediated or a modified Fischer-Tropsch pathway. The selectivity in the latter is strongly limited by the Anderson-Schulz-Flory distribution[3]. An efficient catalyst for methanol-mediated CO_2 hydrogenation to olefins is bifunctional and should be active for both methanol synthesis and methanol dehydration/coupling under the same conditions[3,4]. The goal of this work is to investigate the effect of gallium oxide incorporation into an In_2O_3/SSZ-13 bifunctional catalyst on the formation rate of ethylene and light olefins in methanol-mediated thermo-catalytic CO_2 hydrogenation.

Experimental/methodology

Mixed oxides composed of In_2O_3 and Ga_2O_3 at desired ratios were prepared by coprecipitation, using aqueous solutions of their respective nitrate hydrate salts. The precipitates were aged, filtered, washed with deionized water, dried and then calcined. Both metal oxides and SSZ-13 zeolite were crushed and grinded separately. Then they were physically mixed.

Crystallinity and phases of the samples were analyzed by XRD. Electronic properties and surface oxygen vacancy concentrations were analyzed by XPS. Textural properties of the catalysts were retrieved from N_2 sorption experiments. H_2-TPR was conducted to check the reducibility of the samples. Solid-state NMR was conducted to check the local coordination in the metal oxides. Catalytic performance results were acquired from a microreactor coupled with a gas chromatography.

Results and discussion

The effect of Ga_2O_3 content in an In_2O_3/SSZ-13 bifunctional catalytic system is investigated by performing CO_2 hydrogenation experiments with different Ga-In ratios in the mixed oxides at 20 bar. It was found that increasing Ga/In ratios leads to increase in selectivity of hydrocarbons with shorter chains, tuning the product distribution mainly towards C_2-C_4 product range. More specifically, the ethylene formation rate was greatly enhanced with higher x values of $Ga_xIn_{2-x}O_3$. Placement of indium and gallium species throughout the catalysts and their distributions were mapped by STEM-EDX. Ga^{3+} is incorporated into the In_2O_3 lattice as XPS confirmed. The specific surface area increases with increasing gallium oxide content. NMR results indicated coordination environment pattern of the mixed oxides.

A strong correlation between product type evolution and bifunctional catalyst structure was observed. This work will give an insight in how CO_2 hydrogenation products are tuned towards double bond functionalization by the catalyst design.

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Catalytic conversion of CO_2 to DMC using CeO_2-based catalysts: Optimization study and artificial neural network modelling

P. Kumar[1*], R. Kaur[2], S. Verma[3], U.L. Štangar[1]

[1] *Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia*
[2]*Laboratory for Open Systems and Networks, Jožef Stefan Institute, 1000 Ljubljana, Slovenia*
[3]*School of Energy & Environment, Thapar Institute of Engineering & Technology, Patiala 147004, Punjab, India*
[*]*Corresponding Author's E-mail address - Praveen.Kumar@fkkt.uni-lj.si*

Keywords: CO_2 conversion, M(Mn, Zr)/CeO_2 catalysts, Dimethyl carbonate, ANN modelling, Gibbs energy

Introduction. Carbon dioxide (CO_2) is predominantly discussed negatively as a greenhouse gas and the main cause of anthropogenic climate change. Recently, CO_2 has received more attention as an abundant carbon source and readily available raw material for the production of value-added products, rather than being treated as an environmentally harmful greenhouse gas. In recent decades, the use of CO_2 has attracted the attention of scientific groups, especially those concerned with industrial and environmental processes. In this direction, CO_2 has recently been used as a renewable C1 feedstock for high-value chemicals. Among the various strategies, the carbonylation of alcohols with CO_2 is attractive for the synthesis of dimethyl carbonates (DMC) [1].

Experimental/methodology. The synthesis of CeO_2-based catalysts using a template approach to convert CO_2 to DMC. The relationships between the structure of M(Mn, Zr)/CeO_2 and their catalytic activity have created a need for new synthetic routes for improved surface properties. These synthetic routes are more industrially applicable due to higher activities and lower costs. The effects of the M(Mn, Zr)/Ce molar ratio on the surface properties and structure of the M(Mn, Zr)/CeO_2 catalyst, reaction conditions, and catalyst reusability study for direct conversion of CO_2 were investigated.

Results and discussion. The catalytic activity of the synthesized M(Mn, Zr)-CeO_2 catalysts was closely related to the basic and acidic sites. The optimization of reaction conditions was investigated for various reaction parameters. The reusability of CeO_2-based catalysts was also investigated. In addition, the heat of the reaction and Gibbs free energy were determined using an equation of state (Peng-Robinson-Stryjek-Vera (PRSV-EoS)) with a one-fluid (van der Waals) reaction condition. DMC yields from the direct conversion of CO_2 and methanol in the presence of M (Mn, Zr)/CeO_2 catalysts. Moreover, the experimental response data were validated by the developed artificial neural network (ANN) model [2]. The ANN model was tested by direct comparison and parity plots. The parity plots compare the actual and predicted value of DMC yield. For all data points, the predictions of the ANN model were found to be quite close to the experimental results. The nature of the input data indicates that the model is able to effectively predict the CO_2 conversion and DMC yield under the reaction conditions studied. The parity plots are used to evaluate the over- and under-prediction of the model. The results presented are promising and useful for identifying the key relationships between reaction conditions and targeted performance. This can help in the development of efficient design or screening for heterogeneous catalysts with desired properties.

Acknowledgments

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Epoxidation of CO_2-based light olefins as a key step to fossil-free polycarbonate polyols

K. Kuutti[1*], M. Alvear[2], F. Orabona[2], T. Salmi[2], S. Rautiainen[1], J. Lehtonen[1]
[1]*VTT Technical Research Centre of Finland Ltd, Espoo, Finland*
[2]*Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Turku/Åbo, Finland*
[*]*krista.kuutti@vtt.fi*

Keywords: epoxidation, green chemicals, CO_2 utilization

Introduction. Carbon Capture and Utilization (CCU) technologies enable industrial waste-stream carbon dioxide circulation for value-added products.[1] VTT is currently developing a concept (Figure 1) where polycarbonate polyols are produced from CO_2 and renewable power. In our concept, 100 % of the polyol carbon originates from CO_2, that can be captured e.g. from bioenergy production facilities (BECCU). First, carbon monoxide is produced by a combination of rWGS reaction and catalytic partial oxidation (CPOX). Then, carbon monoxide and hydrogen undergo Fischer-Tropsch (FT) synthesis using a proprietary Fe-based catalyst leading to a high yield (> 45 %) of light C2-C4 olefins.[2] The produced light olefins are further oxidized with hydrogen peroxide into a mixture of epoxides, which are co-polymerized with CO_2 and a starter polyol into polycarbonate polyols to be applied for polyurethanes. However, light olefins are typically epoxidized separately and an industrial process for their combined epoxidation does not exist yet.[3] A direct mixed epoxidation step would bypass the need for challenging and expensive olefin separation, and thus contribute to significant process intensification. This work focuses on the experimental work of liquid-phase epoxidation of light olefins using commercial and in-house synthetized heterogeneous catalysts and hydrogen peroxide as an environmentally friendly oxidant in a continuous flow reactor system. The process concept is shown in Figure 1.

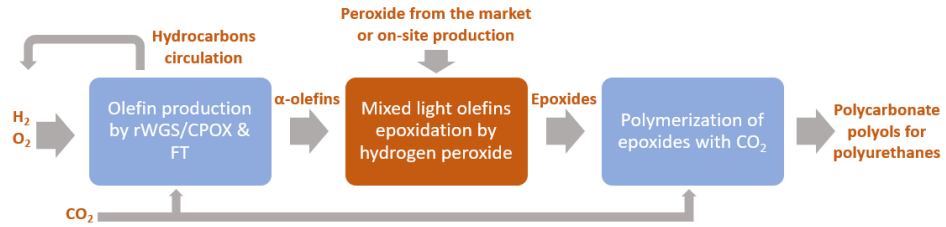

Figure 1. Concept from CO_2 and green hydrogen to polycarbonate polyols.

Experimental/methodology. Liquid-phase epoxidation experiments of mixed light olefins in a fixed bed reactor by hydrogen peroxide on porous silicate supported metal catalysts were performed in a continuous fixed bed reactor. The experiments were conducted under mild conditions using an appropriate solvent (methanol or acetonitrile). The catalysts screened were commercial titanium silicate TS-1, in-house acid-modified TS-1 and two in-house synthetized mesoporous silicate supported catalysts; Nb-KIT-10 and W-KIT-6. The analysis of the epoxidation products was conducted by gas chromatography. The catalysts were characterized by nitrogen physisorption, SEM, EDS and ICP-OES.

Results and discussion. A comparison of the olefins revealed differences in their reactivities. On the other hand, the reactivities of the olefins in the mixtures were surprisingly similar to the olefins tested individually. Furthermore, the product selectivity towards the epoxide product was highly dependent on the process temperature and residence time in the flow reactor. Nonetheless, high selectivities of the corresponding mixed epoxides can be achieved with careful process optimization. Some in-house catalysts gave better performance compared to the commercial TS-1 catalyst.

Acknowledgments

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Direct CO_2 hydrogenation to long-chain hydrocarbons via methanol

F. Lappa[1,2], M. Dusselier[1], G. Leonard[2]

[1]*KU Leuven, Leuven, Belgium*
[2]*ULiege, Liege, Belgium*
[*]*foteini.lappa@kuleuven.be*

Keywords: Carbon dioxide, hydrogenation, methanol, gasoline, heterogeneous catalysis, zeolite, oxide

Introduction. Carbon capture and utilization, CCU, is gaining attention due to the energy crisis and the environmental problems that our society is facing. In particular, CO_2 can react towards long-chain hydrocarbons via two main pathways. First, the Fischer-Tropsch synthesis is an industrialized process based on carbon chain growth, traditionally using CO as a starting point, which is thus the main intermediate from CO_2. On the other side, CO_2 can react towards methanol which is then sent to a Methanol to Gasoline unit (MTG). Not a lot of research has be done in combining CO_2-to-methanol with MTG targeting longer hydrocarbons despite the potential benefits of a direct pathway. As the state of the art indicates, In_2O_3 [1] and $ZnZrO_x$[2] are commonly used for the production of methanol from CO_2. Regarding MTG, zeolites are famous to catalyze this reaction [3]. The combination of both processes in one step reaction still remains quite a challenge, both from catalyst development as from process design points of view.

Experimental. A series of oxides were synthesized ZnZrOx[2], PdZnZrOx[4], Co/In_2O_3, InCo [5,6] and PdInCoOx. Medium and large-pores zeolites were tested such as TON, ZSM-5 and BEA. Si/Al ratio variations and the effect of the acidity were studied. All materials were characterized with XRD and BET, ICP (Si/Al ratio), NH_3-TPD and FTIR. In addition, different bed configurations are under study.

Results and discussion. Fig 1. shows that ZnZr-oxides and InCo are methanol production catalysts. When tested without the presence of zeolite the main product was methanol. When combined with BEA zeolite, paraffins are the main product and this effect is enhanced for the dual bed configuration. Large pores zeolites such as BEA have the possibility to allow longer-chain hydrocarbons to escape the pores. In dual bed, methanol is first produced in the oxide layer and then converted to hydrocarbons in the BEA layer. This first screening sets the stage for investigating other zeolites as well the effect of the acidity and other synthetically accessible properties of BEA zeolites in this reaction. The main aim is to map the effects of the CO_2 hydrogenation conditions, especially high partial pressures of CO_2 and water and a reducing environment, on the selectivity and long alkane MTG performance of the zeolite.

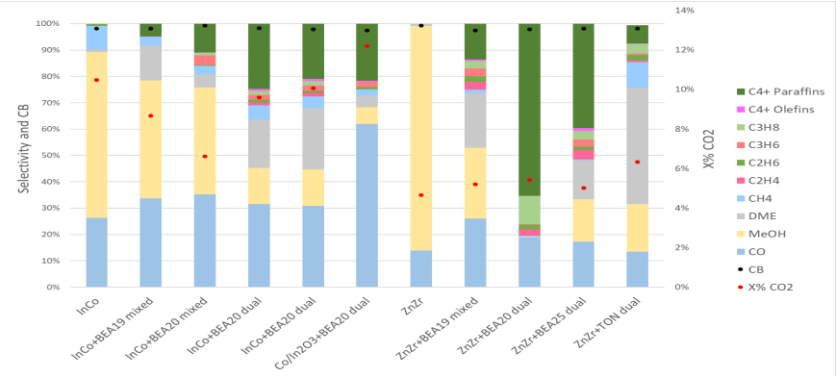

Fig1. CO_2 conversion, carbon balance (CB) and selectivity of products in the presence of different catalytic materials.

Acknowledgments
With the financial support of the Energy Transition Fund

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Ni/CeO_2-ZrO_2 catalysts for dry methane reforming – optimization of nickel loading and support composition

P. Legutko[1*], W. Pierożak[1], I. Poniewierska[1], S. Kuler-Rachwał[1], M. Kozieł[1], M. Marzec[2], M. Michalik[3], A. Adamski[1]

[1]*Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland*
[2]*ACMiN, AGH University of Science and Technology, Mickiewicza Ave. 30, 30-059 Kraków, Poland*
[3]*Institute of Geological Sciences, Jagiellonian University, Gronostajowa 3a, 30-387 Kraków, Poland*
[*]*piotr.legutko@uj.edu.pl*

Introduction. In recent years, the efficient reduction of the emission of GHGs into the atmosphere became one of the most important scientific and societal challenges worldwide. Satisfactorily, the solutions proposed by environmental catalysis seem to meet the expected goals One of the possible technological options oriented towards effective CO_2 utilization is its conversion into synthesis gas. The target mixture can be catalytically obtained in the reaction called dry reforming of methane (DMR): $CH_4 + CO_2 \rightarrow 2CO + 2H_2$. The DMR is a highly endothermic reaction, so a high temperature and an active catalyst are indispensable to gain satisfactory conversion and selectivity. A lot of investigations were performed to develop a promising catalytic system such as Ni/CeO_2-ZrO_2, but the effect of active component loading is still not fully explained. This study aimed to understand in-depth and to elucidate the influence of both nickel content and support phase composition on the physicochemical properties and catalytic activity of Ni/CeO_2-ZrO_2 catalysts active in DMR.

Experimental/methodology. CeO_2-ZrO_2 support (containing 0-100% ZrO_2) was synthesized by the Pecchini method from cerium(III) nitrate(V), citric acid and ethylene glycol. The obtained gel was dried overnight at 120 °C and then calcined at 800 °C for 6 h. Final catalysts were prepared by impregnation of the binary support with nickel nitrate(V) solutions (0 – 10 wt.% of Ni). After impregnation, all samples were dried overnight at 120 °C and then calcined at 400 °C for 3 h to decompose the precursor. Subsequently, the samples were characterized by XRD, RS, SEM, XPS, DRIFT and UV/Vis-DR. The catalytic activity of reduced samples (5% H_2/Ar, 2h) has been investigated in the temperature range 550-800 °C with the composition of gases: 2.5% CH_4 and 2.5% CO_2 in He.

Results and discussion. The obtained results showed that optimal nickel loadings can be determined for all support compositions and it was shifted from 3 wt.% of active phase supported on bare CeO_2 (see Fig. 1) to around 5% for mixed supports and 10% for bare ZrO_2. Moreover, it was found that optimal loading can be different for the same support composition but with different synthesis methods. In general, activity and stability optima are in the same Ni concentration but in some cases, higher nickel loading results in stability enhancement. Investigated Ni/CeO_2-ZrO_2 catalysts meet most of the DMR requirements and their effective optimization is also helpful for large-scale application designing.

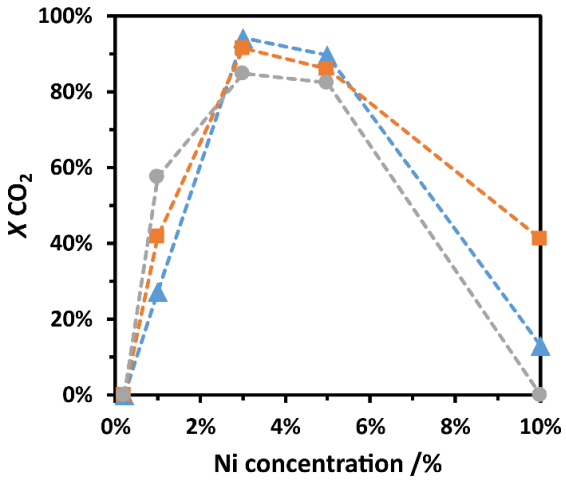

Fig. 1. Catalytic activity expressed as CO_2 conversion observed during DMR process as a function of nickel loading in Ni/CeO_2 catalyst: at 700 °C (circles), at 750 °C (squares), and at 800 °C (triangles).

Acknowledgments

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CO_2 Reduction to Methanol at a Cu/Zn–ZrO_2 Interface via DFT Calculations

A. Lempelto[1*], L. Gell[1], T. Kiljunen[1], K. Honkala[1]

[1]*University of Jyväskylä, Nanoscience Center, Jyväskylä, Finland*
[*]*aku.p.lempelto@jyu.fi*

Keywords: Heterogenous catalysis, Density Functional Theory, CO_2 utilisation

Introduction. A combination of Cu/Zn/ZrO_2 has been found to efficiently catalyse CO_2 conversion to methanol (CTM) [1,2]. It has been suggested that the Cu and Zn components can form a partial alloy under reaction conditions although this interpretation remains controversial [3,4]. Previous computational studies have mainly focused only on binary systems of Cu-ZnO or Zn-ZrO_2.

Experimental/methodology. We have studied the CTM capabilities of the CZZ system using density functional theory (DFT) calculations and zirconia-supported periodic Cu nanorod models, similar to those in our previous work [5], with some or all interfacial Cu atoms replaced by Zn. A simple kinetic analysis of DFT results was done using the energetic span model [6,7] in order to identify TOF controlling states.

Results and discussion. Our results demonstrate that CO_2 hydrogenation intermediates binding to interfacial metal atoms adsorb more strongly to Zn sites than to geometrically equivalent Cu sites at the metal—support interface where the active sites lie. We show that the promoter has little effect on the binding of intermediates which are not in direct contact with the metal component of the system, including some key intermediates identified with the ESM analysis such as the formate and methoxy. Additionally, the results have highlighted the importance of considering hydrogen spillover in computational studies. We show that by including hydrogen spillover, the activation energies for some hydrogenation reaction steps involving zirconia-bound intermediates are much lower than previously reported. These effects lead to an energetic preference for the so-called reverse water—gas shift (RWGS) route of CO_2 hydrogenation (yellow in Fig. 1). Our results therefore help quantify the effect of metallic Zn sites on catalytic properties such as selectivity.

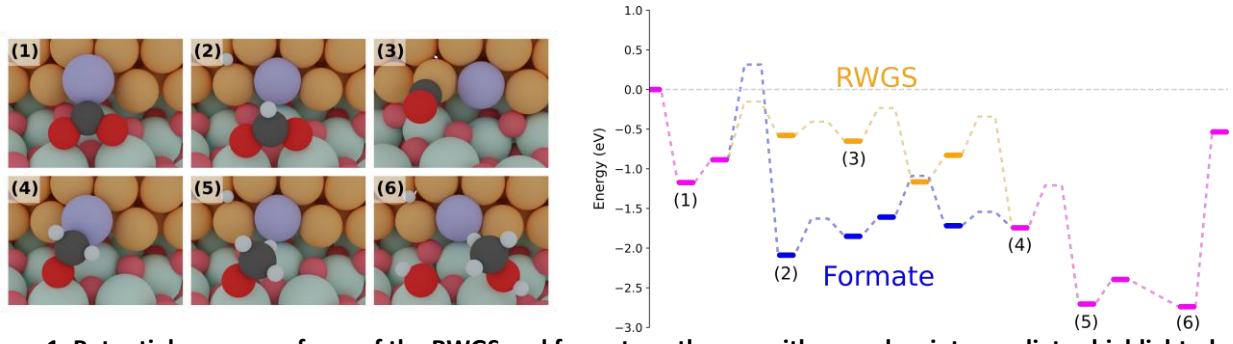

Figure 1. Potential energy surfaces of the RWGS and formate pathways with some key intermediates highlighted.

Acknowledgments

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CO_x hydrogenation to methanol on supported Cu NPs: role of electron withdrawing character of Lewis acid sites at metal/oxide periphery

I. López-Luque[1], J. Kim[2], G. Prieto[1,2,*]

[1]*ITQ Instituto de Tecnología Química (CSIC-UPV), Valencia, Spain.*
[2]*Max Planck Institute KOFO, Müllheim an der Ruhr, Germany.*
[*] *Email: prieto@itq.upv.es*

Introduction.
Cu-based catalysts are industrially applied to convert syngas mixtures (CO_2/CO/H_2), while the conversion of single-carbon-oxide CO_2/H_2 and CO/H_2 feeds attracts increasing attention in the context of emerging power-to-X technologies. Despite the established character of these catalyst systems for methanol synthesis, the nature of the metal-oxide promotion effects, as well as the prevailing reaction mechanism and optimal catalyst design for CO_2 vs CO hydrogenation, remain open scientific questions.[1] Herein, we extend our studies on the mechanistic role of the electron withdrawing character (acidity) of Lewis acid sites (LAS) at the Cu/oxide periphery,[2] as a means to rationalize mechanistic similarities and differences for CO_2 and CO hydrogenation reactions.

Experimental/methodology.
A series of model catalysts consisting of Cu nanoparticles dispersed on various transition metal oxide overlays coated on a common γ-Al_2O_3 substrate (1.5Cu_{at}/MO_x@Al_2O_3, MO_x, M=Ta, Zr, Sc and Y) was synthesized as reported earlier.[2] Methanol synthesis tests were performed with H_2/CO_2=3 or H_2/CO=2 feeds at WHSV=1-3 h^{-1}, T=503-523 K, and P=25 bar.

Results and discussion.

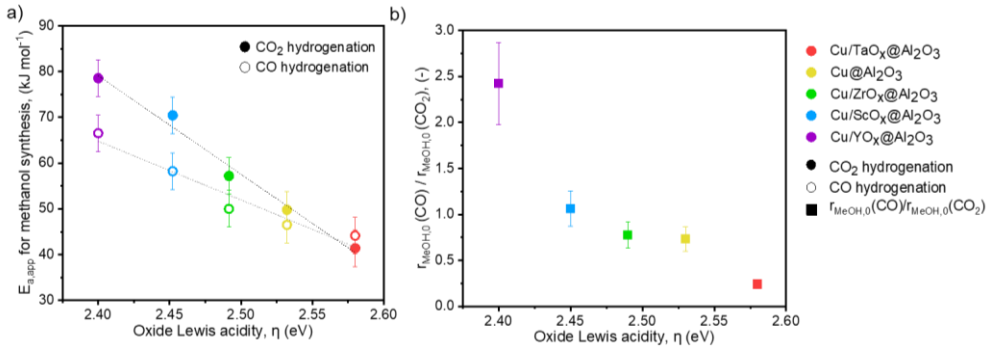

Figure 1: Evolution of a) the apparent activation energy for methanol formation, and b) ratio of initial methanol formation rates for CO/H_2 and CO_2/H_2 feeds at 513 K, as a function of the relative electron withdrawing character of the oxide support LAS (quantified by the IMCT energy of adsorbed 1,2-dihydroxy-9,10-anthracenedione as probe (η)).

Independently from the identity of the carbon oxide in the feed, the apparent activation energy for methanol formation decreased rather linearly with increasing the electron withdrawing character of the *cus* on the oxide support (Fig. 1a). These comparable trends for E_{app} suggest a mechanistic parallelism for the hydrogenation of both CO_x, i.e. in both cases, LAS (likely at the Cu/oxide periphery) are involved in a kinetically relevant step which becomes facilitated by LAS with stronger electron withdrawing character, particularly so for CO_2 hydrogenation. However, reaction rates did show remarkable differences for CO_2 and CO feeds (Fig. 1b), suggesting differences in either TOF or the number of active sites at work. Oxides of stronger electron withdrawing capacity are notably more effective hydrogenating CO_2 than CO and vice versa. Isotopic H/D exchange and *in situ* FTIR studies provide complementary insights into the mechanistic similarities and differences for methanol synthesis reactions by hydrogenation of the two carbon oxides.

Acknowledgments
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Photo-thermal methane dry reforming reaction catalyzed by Ni/CeO_{2-x} nanorods

Kristijan Lorber[1,2], Iztok Arčon[2], Petar Djinović[1,2*]

[1] *National Institute of Chemistry, Ljubljana, Slovenia*
[2] *University of Nova Gorica, Vipavska, Slovenia*
[*] *petar.djinovic@ki.si*

Keywords: DRM, nickel, ceria, photo-thermal catalysis, operando DRIFT

Introduction.
The dry reforming of methane (DRM) reaction represents an effective way of utilization two major greenhouse gases into syngas, but it is highly endothermic and thermodynamically limited reaction (CH_4 + CO_2 ↔ H_2 + CO; ΔH_{298K} = +247 kJ/mol).[1],[2] Implementation of visible light into thermally driven DRM reaction is an attractive alternative for surpassing the thermodynamic equilibrium limits and achieving high catalytic activity and selectivity at low temperatures.[3] The aim of this work is to determine how calcination in different atmospheres (oxidative, inert and reductive) affects on activity of nickel-ceria based catalysts during thermal, as well as photo-thermal DRM reaction. Furthermore, detailed insight studies were performed to elucidate the photo effect on catalytic performance regarding DRM reaction.

Experimental/methodology.
The catalysts based on ceria rod morphology were synthesized by hydrothermal treatment, whereas 2 wt. % of nickel as active metal was loaded by deposition precipitation method.[4] The samples were separately calcined in different atmospheres, namely Air, Ar and H_2 before and after the deposition of Ni. All catalytic tests for thermo and photo-thermal DRM reaction were performed in modified Harrick reaction chamber (HVC-MRA-5) at ambient pressure.[3] The same reaction chamber combined with microGC analysis were also used to perform *operando* DRIFTs analysis, using a Perkin Elmer IR spectrophotometer. The visible light used during photo-thermo conditions was provided by Schott KL2500 LED source (400 <λ< 700 nm) with the intensity of 613 mW/cm^2.

Results and discussion.
Under thermal conditions, the best performing catalysts are 2Ni-R H_2 and 2Ni-R Ar, followed by 2Ni-R Air. When the reaction is thermally driven, no activity is observed below 380°C. With introduction of concentrated visible white light, the catalytic activity and H_2 selectivity further increased in case of all studied catalysts as well as the catalytic reaction was extended to 140°C. The photocatalytic gains in CH_4 and CO_2 rates and H_2 selectivity become more prominent over 2Ni-R H_2 and 2Ni-R Ar compared to 2Ni-R Air catalyst. Furthermore, the most dominant impact on observed CH_4 as well as CO_2 photocatalytic activity has the hot charge-carrier driven photocatalytic mechanism (PT). The provided operando DRIFTs analysis reveals that introduction of visible light promotes the photocatalytic oxidation of formate species to CO, therefore preventing them to further hydrogenate into CH_4. Moreover, visible light also induces removal of carbonyl groups from nickel, meaning more active sites are available for methane dissociation. Based on the *in-situ* XANES/EXAFS measurements, higher Ni dispersion was noticed on samples calcined in inert and reductive atmospheres compare to the sample calcined in air. Overall, the improved dispersion of Ni by calcination in inert or reductive atmospheres is the main factor for enhancement in catalytic activity during DRM reaction under thermal and photo-thermal conditions.

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Efficient use of oxygen atoms in photocatalytic CO_2 reduction

Peng Bai[1], Yicheng Zhao[1]*, Yongdan Li[2]

[1]*Department of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*
[2]*Department of Chemical and Metallurgical Engineering, Aalto University, Kemistintie 1, FI-00076 Aalto, Finland*
**E-mail for Yicheng Zhao: zhaoyicheng@tju.edu.cn*

Keywords: BiOBr, CO_2 reduction, g-C_3N_4, Oxygen atoms, Photocatalysis

Introduction. Photoreduction of CO_2 to fuels is promising to mitigate climate warming and increase the renewable energy supply, while conventional photocatalytic CO_2 reduction systems with H_2O or sacrificial agents generally face problems such as low catalytic activity and inefficient atom economy[1,2]. In this work, NH_4Cl-modified g-C_3N_4 is combined with BiOBr for the efficient photocatalytic CO_2 reduction coupled with selective styrene oxidation. The interfacial heterostructure promotes the formation of surface amino groups and oxygen vacancies, which facilitates the adsorption and chemical reduction of CO_2, and also improves the separation of photogenerated electron-hole pairs and enhances the photocatalytic activity. Compared with the conventional CO_2 reduction process where oxygen atoms removed from CO_2 are converted to the no added valuable H_2O or O_2 destroyed the reduction system[3], in our synergistic system, the oxygen atoms are efficiently involved in the styrene oxidation half-reaction. This study provides a novel strategy for designing high-efficient photocatalytic CO_2 reduction system and new insights into the reaction mechanism.

Experimental/methodology. 0.1 mmol styrene, 10 mg photocatalyst and 5 mL acetonitrile were added in a 50 mL autoclave with a glass window. The light source was a CEL-HXF300 Xe lamp (Beijing China Education Au-light Technology Co., Ltd) with a light density of 43 $mW \cdot cm^{-2}$. The photocatalytic redox reaction was carried out in a CO_2 atmosphere (0.1 MPa) under magnetic stirring at room temperature for 3 h. The CO_2 reduction products were analyzed using a GC (Fuli GC979011) with a flame ionization detector (FID) and thermal conductivity detector (TCD). The styrene oxidation products were qualitatively analyzed with a gas chromatograph-mass spectrometer (GC-MS, GC-Agilent 6890A) and quantitatively analyzed using a GC (Shimadzu, Japan) with a flame ionization detector (FID) and an SH-Rtx-1 capillary column (30 m×0.25 mm×0.25 μm).

Results and discussion. The BiOBr-NCN heterojunction catalyst is constructed to achieve efficient oxygen atom utilization in the photocatalytic CO_2 reduction by coupling with styrene oxidation at room temperature. The heterostructure facilitates the formation of surface amino groups and oxygen vacancies, which is beneficial to the adsorption and chemical reduction of CO_2. The heterostructure also improves the separation efficiency of photogenerated charge carriers and enhances the photocatalytic response. The simultaneous consumption of photogenerated electrons and holes is favorable to both the reduction and oxidation half-reactions. A high CO generation rate of 802 μmol g^{-1} h^{-1} with a 96.2% selectivity is achieved, and the production rates of benzaldehyde and styrene oxide are 684 and 139 μmol g^{-1} h^{-1}, respectively. A novel mechanism is proposed based on the results of in situ FTIR, in situ EPR, isotope tracer and control experiments, and the BiOBr-NCN heterostructure sample also shows good cycling stability and universality.

Acknowledgments
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Mn-Ni dual-atom sites for efficient electroreduction of CO_2 to CO

S. Lu[1], F. L. Lou[2], Z. X. Yu[1*]

[1]*Department of Energy and Petroleum Engineering, University of Stavanger, Stavanger, Norway*
[2]*Beyonder AS, Stavanger, Norway*
zhixin.yu@uis.no

Keywords: Electrocatalysis, Carbon dioxide conversion, dual-atom catalysts, Mn−Ni site

Introduction

The electrochemical reduction of CO_2 (ECR) into value-added products provides a promising strategy to realize a carbon-neutral energy [1]. However, the current ECR process still has challenges of CO_2 activation and the complicated product distribution, which limits practical CO_2 reduction. Therefore, it is deisrable to develop electrocatalysts with good activity and high selectivity for ECR. Single-atom catalysts (SACs) have demonstrated appealing performance for ECR to CO due to high atomic efficiency, unique geometric and electronic structure [2]. However, the simplicity of active center limits the efficiency of catalytic reaction due to the multistep-coupled proton-electron transfer of ECR process. For instance, Ni SACs generally show excellent CO desorption capability and suppression of HER, whereas suffer from sluggish kinetics of the first proton-coupled electron transfer [3]. Fe SACs exhibit low free energy barrier for the formation of *COOH intermediate, but the CO desorption from active site is diffcult because of strong binding of CO to Fe atom [4]. To solve these issues, one strategy is to construct diatomics site with unique geometric and electronic property by incoporating extra heteronuclear metal atoms into SACs.

Experimental/methodology

Five catalysts including Ni−N−C, Mn−N−C, Ni−Ni−N−C, Mn−Mn−N−C and Mn−Ni−N−C supported on N-doped carbon black were synthesized via a facile ion adsorption and calcination process.

Results and discussion

The catalysts were charactered by XRD, Raman, HRTEM, HAADF-STEM, XANES, EXAFS, XPS, N_2-physisorption, etc. XRD results indicated that there are no Ni and Mn metallic clusters or compounds in the Mn−Ni−N−C catalyst (Fig. 1a). EDX mapping revealed that Mn, Ni, N, and C species distribute uniformly over the Mn−Ni−N−C catalyst. XPS results suggest that the Ni and Mn species are likely to be in a partially oxidized state. The atomically dispersed Ni and Mn species were verified by HAADF-STEM as shown in Fig. 1b. Finally, the Mn−Ni−N−C catalyst exhibits the highest ECR activity, yielding a current density of 17.1 mA/cm² under −0.70 V (vs. RHE) and maximum FE(CO) of 98.7% (Fig. 1c).

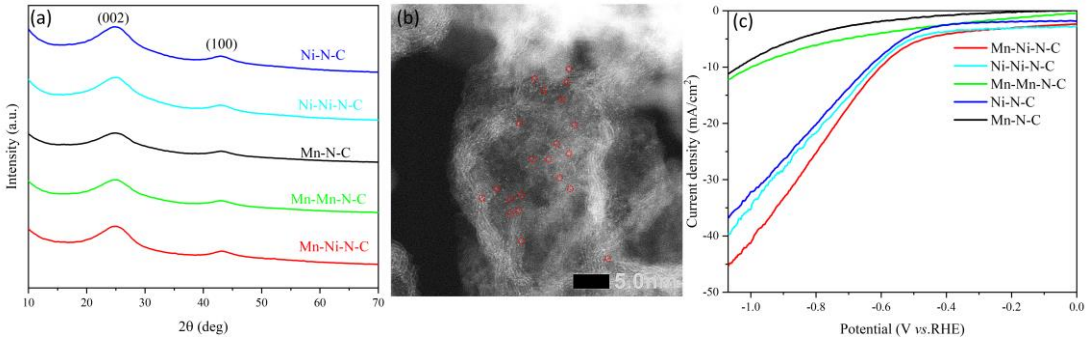

Figure 1. (a) XRD patterns of the five catalysts; (b) HAADF-STEM of the Mn−Ni−N−C catalyst, where Mn-Ni atom pairs are highlighted in red circles; (c) LSV of the catalysts.

Acknowledgments

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Zeolitic Imidazolate Frameworks as co-catalysts for CO_2 gas-phase photo-reduction

C. Marchal[1*], M. Anagnostopoulou[1], K.C. Christoforidis[2], V. Keller[1]

[1]ICPEES-*Institute of Chemistry and Processes for Energy, Environment and Health, UMR 7515, CNRS/University of Strasbourg, Strasbourg, France*
[2]*Department of Environmental Engineering, Democritus University of Thrace, Xanthi, Greece*
[*]*cle.marchal@unistra.fr*

Keywords: ZIF-8, ZIF-67, ZIF-8@ZIF-67, TiO_2, Heterojunction, CO_2 photoreduction

Introduction. CO_2 photoconversion appears as a very promising way to answer to the environmental crisis that human are facing. Titania is one of the most studied semiconductor for CO_2 photoreduction but one of the main issues is the lack of efficiency. Indeed, the gas-phase photocatalytic CO_2 reduction by H_2O over titania leads to the formation of hydrogen as preferential/competitive process, limiting the overall CO_2 reduction yields and the selectivity. In order to avoid this phenomena, the use of suitable co-catalyst appears as a promising way to control TiO_2 photoactivity and selectivity toward CO_2 reduction.

Experimental/methodology. ZIFs materials were prepared in aqueous media [1-2]. 1.4667 g of zinc nitrate ($Zn(NO_3)_2.6H_2O$) was dissolved in 100 mL of MeOH. 3.2647 g of 2-methyl imidazole was also dissolved in 100 mL of MeOH. The second solution was added dropwise and strirred for 2 hours, the sample was washed with MeOH and distilled water and finally vacuum dried at 80°C overnight. The same procedure was apllied for ZIF-67 using cobalt nitrate ($Co(NO_3)_2.6H_2O$) as metal precursor. Composite materials were obtained via wet impregnation between TiO_2 and ZIF materials.

Results and discussion. The photocatalytic measurement were done using a gas phase reactor under simulated sunlight and continuous flow (0.3 mL/min) (**Figure 1**). One can observe that increasing the amount of ZIF materials from 1 to 10 wt.% leads to the preferential formation of C-compounds compared to the production of H_2 with a full C-compound selectivity obtained using ZIF-8@ZIF-67 as co-catalyst.

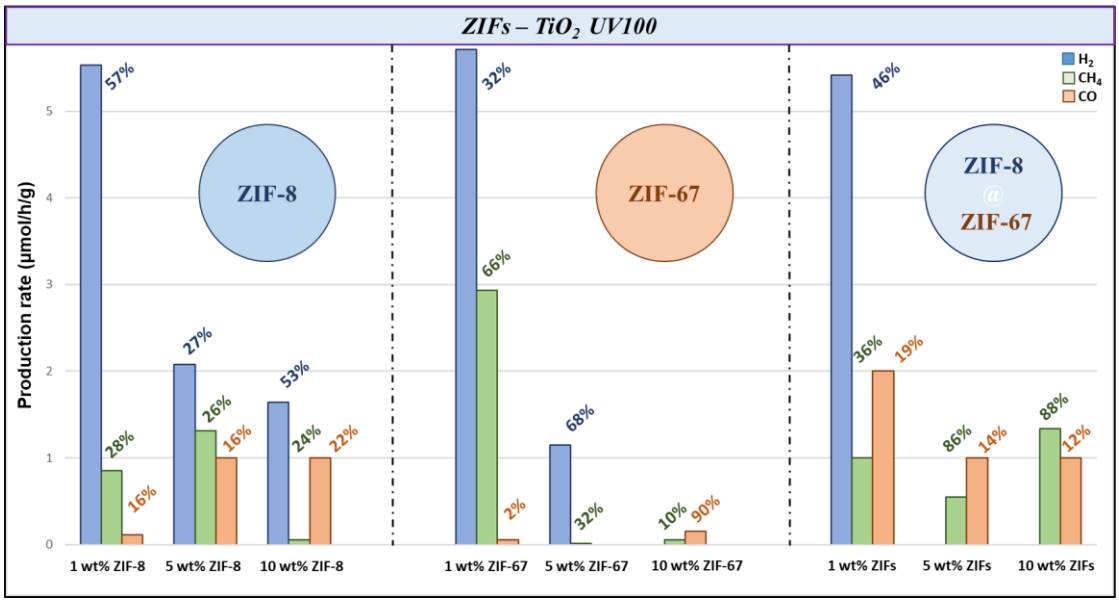

Figure1: CO_2 photoreduction over ZiF/TiO_2 materials

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CO_2 Reduction to Syngas over Mo_2C-Based Catalysts

W. Marquart, M. Claeys and N. Fischer*

*Catalysis Institute and DSI-NRF Centre of Excellence in Catalysis c*change, University of Cape Town, Cape Town, South Africa*
**nico.fischer@uct.ac.za*

Keywords: CO_2 reduction, molybdenum carbide, synthesis gas, Power-to-X

Introduction. The widely discussed Power-to-X (PtX) processes [1] assume that the renewable energy sector will grow significantly over the coming years resulting in very cheap electricity at times of high production and low consumption. This essentially free electricity provides opportunities such as the large-scale electrolysis of water yielding H_2 and a subsequent hydrogenation of captured CO_2 to so called hydrocarbon based powerfuels, especially in the aviation sector which is unlikely to be directly electrified. A first step in this process is the activation of CO_2 with H_2 in the reverse water-gas-shift (RWGS) reaction to CO. Due to its thermodynamically limited conversion even at very high reaction temperatures, the RWGS represents a significant challenge in the PtX process to powerfuels both regarding catalyst stability and performance. Molybdenum carbides (Mo_2C) have been shown to be promising candidates for the activation of CO_2 [2].

Experimental/methodology. The present study investigates the performance of various Mo_2C-based catalysts under RWGS conditions. The catalysts are prepared via a common slurry impregnation method on various metal oxide support materials, with the carburization process being optimized using several *in situ* characterizing techniques, such as XRD, Raman, XAS and TGA-MS. To obtain an active and stable catalyst, it is important to limit the carbon build up on the surface of the catalyst during carburization of the precursor materials but still obtaining a pure carbide phase without oxidic species. The obtained catalysts were tested in a ¼" tubular fixed bed reactor, varying feed gas composition and space velocity.

Results and discussion. Our results indicate that the optimum temperature for a pure phase carburization of ammonium heptamolybdate (AHM) supported on conventional fumed silica is 600°C, according to *in situ* XRD. *In situ* Raman analysis confirms that at these conditions no significant carbon deposition has taken place and no surface oxidic phases (MoO_x) are present. In terms of the RWGS performance (see Figure 1), the catalysts were evaluated for 24 hours at 600°C using a H_2 to CO_2 feed at a ratio of 2.5. Limited catalyst deactivation can be observed for all catalysts. The conversion level of the Mo_2C-based catalysts is heavily influenced by the support material. The inert SiO_2 support is the best performing catalyst, suggesting that Mo_2C can fully support the CO_2 activation as well as the subsequent oxygen removal by H_2, forming H_2O, on its own. The selectivity towards CO is approaching 100 C-% for all catalysts, confirming that there is no significant CO or CO_2 methanation taking place. Mo_2C promises to be an active, effective and cost efficient (compared to PGM alternatives) catalyst for the RWGS reaction.

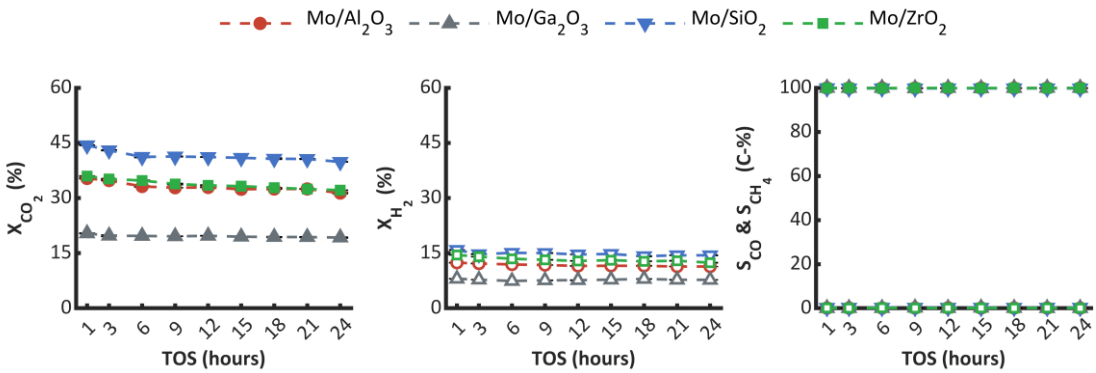

Figure 1. CO_2 and H_2 conversions as well as CO and CH_4 selectivity of the metal oxide support Mo catalysts under RWGS conditions.

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Perovskite-based catalysts for CO_2 photoreduction reaction

I. Martin[1*], G. Forghieri[2], E. Ghedini[2], I. Rossetti[3], M. Signoretto[2]

[1]*Functional Nanosystems, Italian Institute of Technology, Via Morego 30, 16163 Genoa, Italy*
[2]*Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice and INSTM RU of Venice, Via Torino 155, 30172 Venice, Italy*
[3]*Chemical Plants and Industrial Chemistry Group, Chemistry Department, University of Milan, CNR-SCITEC ans INSTM RU of Milan, Via C. Golgi 19, 20133 Milan, Italy*
[*]*Corresponding Author's E-mail address: irene.martin@iit.it*

Introduction. The worrying rise in greenhouse gas emissions has led to the necessity of limiting the consumption of fossil sources on one hand, and on the other to develop new technologies for capturing, storing and utilising these gases [1]. In this perspective, CO_2 photoreduction, paired with water splitting, presents a great potential for the synthesis of fuels and other building block molecules of high value, *e.g.* methane (CH_4), carbon monoxide (CO) and other C1-based products [2]. To develop an effective and selective photocatalytic system, the perovskite barium titanate ($BaTiO_3$) was chosen as a new promising photoactive material with respect to other common photocatalysts, *e.g.* titanium dioxide (TiO_2) and zinc oxide (ZnO). Copper (II) oxide was introduced as a co-catalysts to hinder charge recombination [3], enhacing the activity and selectivity of the perovskite.

Experimental/methodology. $BaTiO_3$ was synthesized by hydrothermal method, modified from literature [4], and was compared with commercial TiO_2 (Degussa P25, Evonik) and a lab-synthesized ZnO (synthesized by precipitation [5]). CuO was synthesized by hydrothermal method [6] and introduced as a co-catalyst by impregnation (2.5 wt%) on $BaTiO_3$, TiO_2 and ZnO. The photocatalysts were tested in a gas and liquid phase.

Results and discussion. Experiments performed in gas phase resulted in the production of methane and hydrogen, in accordance with the proposed reaction mechanism [7]. Pristine $BaTiO_3$ was less active with respect to TiO_2 (79 vs 104 µmol g_{cat}^{-1} h^{-1} of CH_4, respectively), but the presence of CuO both improved both its activty and resulted in a minor H_2 production with respect to CuO/TiO_2 (221 vs 169 µmol g_{cat}^{-1} h^{-1} of CH_4 and 239 vs 414 µmol g_{cat}^{-1} h^{-1} of H_2, repectively). Experiments performed in liquid phase under neutral pH resulted in the production of formic acid and methanol [7], whereas under basic pH only HCOOH was detected. The basic enviroment also provided a ten-fold total productivity in C-based molecules with respect to pH 7. Under these reaction conditions, the materials showed similar activity and the introduction of CuO did not lead to significant improvements. Thus it is possible to argue that CO_2 photoreduction performed in liquid phase is driven by reaction conditions, whilst in gas phase the choice of the appropriate photocatalyst can redirect the activity and selectivity of the reaction.

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Fe catalysts supported on N-doped graphite and K as a promoter for CO_2 hydrogenation to light olefins

L. Martínez-Quintana[1], E. Castillejos-López[2], J.Rabeah[3], A.B. Dongil[1*]

[1]*Instituto de Catálisis y Petroleoquímica (CSIC), 28049 Madrid, Spain*
[2]*Departamento de Química Inorgánica y Química Técnica, Facultad de Ciencias, UNED, 28040 Madrid, Spain*
[3]*Leibniz-Institut für Katalyse, 18059 Rostock, Germany*
**a.dongil@csic.es*

Keywords: Heterogeneous catalysis, CO_2 valorization, carbon materials, light olefins

Introduction: Carbon dioxide (CO_2) is a greenhouse gas and its increasing concentration in the atmosphere due to anthropogenic activity is related to global warming. For this reason, it is necessary to find efficient and clean processes to transform CO_2 into value-added products, such as light olefins. Light olefins are of great interest in the chemical industry since they are used as raw materials in the production of surfactants, plasticizers, solvents, etc. Usually, iron catalysts are used as they can catalyze the reverse water gas shift reaction (RWGS) over Fe_xO and the C-C coupling via Fischer-Tropsch (FT) over Fe_xC [1]. The present work studies the activity of Fe catalysts over graphite supports doped with potassium and nitrogen for the hydrogenation of CO_2 to light olefins.

Experimental/methodology: The support was a high surface area graphite (Timcal, S_{BET}: 400 m^2/g) impregnated and grounded with melamine (10 wt.% N) and heated at 600 °C for 1 h under N_2 flow. The catalysts were prepared by incipient impregnation using $Fe(NO_3)_3{\cdot}9H_2O$ (15 wt% Fe) and dried overnight at 100 °C. Catalyst pretreatments were: H_2 at 500 °C 2h (Fe/G-N/H_2), CO at 350 °C 4 h (Fe/G-N/CO) and He at 500 °C 2h (Fe/G-N/He). A portion of the catalyst was impregnated with K_2CO_3 (Fe:K molar= 4:1) (Fe(K)/G-N/H_2) and a catalyst not N-doped was also prepared (Fe(K)/G/H_2). The reaction was performed with 350 mg of sieved catalyst at 300 °C and 10 bar using a total flow of 80 ml/min (45% H_2, 15% CO_2, 40% He).

Results and discussion: The characterization of the N-doped support indicated that it has a BET area of 353 m^2/g. The XPS showed a N/C ratio of 0.02, with the main contributions in the N1s region located at 398.3, 399.7 and 400.8 eV attributed to pyridine-N, pyrrole-N and graphite-N respectively. Conversion among N-doped catalyst was similar and higher than that of Fe(K)/G/H_2 (Fig.1), except for the catalyst prepared under inert atmosphere (not shown) with which the conversion was around 6% and 98% selective to CO. Interestingly, small selectivity differences are observed between pretreating the catalyst under H_2 or CO flow, and even the former produces more C2-C4 compared to CH_4. The K-promoted catalyst, Fe(K)/G-N/H_2, showed higher selectivity towards light olefins than Fe/G-N/H_2, while CH_4 and C2-C4 decreased. This agrees with what has been reported: K may favor smaller iron particles, enhances iron carburization, and provides a better yield to light olefins [2]. The characterization of the catalysts by XRD and EPR showed different phases on the fresh catalyst: (Fe (H_2-treated), Fe_xC (CO-treated and Fe_3O_4 for N_2-treated), so ongoing characterization under reaction conditions is being studied to provide more insights into the active phases.

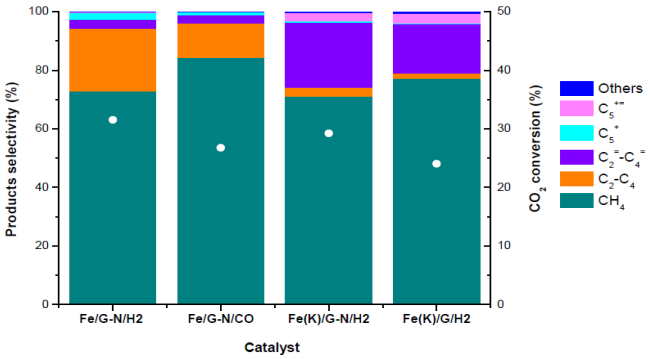

Fig. 1 Conversion and products selectivity of each catalyst (CO selectivity excluded)

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CO_2 valorisation with earth-abundant metals using visible-light

S. Realista, R. T. Marques, N. A. G. Bandeira, R. G. Santos, P. N. Martinho*

Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Ed. C8, 1749-016 Lisboa, Portugal
**pnmartinho@ciencias.ulisboa.pt*

Keywords: carbon dioxide, photoreduction, visible-light, methane, carbon monoxide

Introduction. One of the most important players in molecular activation is carbon dioxide due to its crucial role in the environment with consequences for the climate and heating the earth's surface by trapping infrared radiation in the atmosphere. Unfortunately, the expansion of the human population and the energy demand resulting from there, derived in an increase in carbon dioxide concentration unbalancing the earth's carbon cycle, thus affecting the energy balance of the planet. As a result, scientists have struggled to reduce CO_2 into added-value chemicals such as carbon monoxide, formic acid, methane and methanol that can be used as fuels. Catalysis has been the most attractive approach with a recent scientific interest increase in the catalytic CO_2 photoreduction, as light is a sustainable electron source essential for the conversion – artificial photosynthesis.[1] We have previously reported a metal cryptate that can capture and convert CO_2 into carbon monoxide and methane triggered by visible light and we now aim at transferring this catalytic system from the lab to the pilot scale.[2] To reach this goal we will first optimise the catalytic conditions (eg.: light configuration, catalysts' structure, photosensitiser, etc) at the lab scale.

Experimental/methodology. Preparation of the already published[2] cryptates and new cryptates (Fig. 1) having different aromatic ring substituents (-H, -Br, -I, -CCH, -OMe) and metal centres (Zn^{II}, Co^{II}). Evaluation of their catalytic CO_2 photoreduction to CO and CH_4 performance using blue visible light.

Results and discussion. The aromatic ring substituent and a different metal centre influence the reactivity towards CO_2 photoreduction. We also optimised the photocatalytic system, by introducing a reversible quencher.

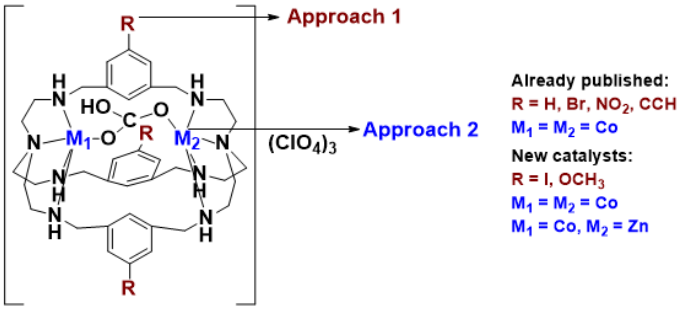

Fig. 1 – Approaches for the optimisation of the cryptates' structure

Acknowledgements

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P.N.M. and S.R. acknowledge FTC for financial support (CEECIND/00509/2017 and (2020.02134.CEECIND). R.T.M thanks for the PhD fellowship within the project PTDC/QUI-QIN/0252/2021.

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FSP-made Ru/SiO_2 and $Ru/Ti\text{-}SiO_2$ catalysts for CO_2 methanation reaction

Okorn Mekasuwandumrong[1], Patcharaporn Jornsamer[1], Kanika Khuon[1],
Nareuporn Suksawang[1], Supareak Praserthdam[2] and Piyasan Praserthdam[2*]
[1] *Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakorn Pathom 73000, Thailand*
[2] *Center of Excellence on Catalysis and Catalytic Reaction, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand*
[*] *E-mail: piyasan.p@chula.ac.th*

Keywords: CO_2; Methanation; Ru; SiO_2; Ti; Flame spray pyrolysis

Introduction.

Recently, CO_2 released from the combustion of fossil fuel are known as the main pollutant that can lead to global warming and climate shift. Thus, it is very necessary to control the CO_2 emission into the air by converting the CO_2 in to value-added compound. Methanation reaction is the reaction that can converts CO_2 and hydrogen, and is a popular method of hydrogen retention which can reduced the CO_2 content [1].

Flame spray pyrolysis (FSP) is a very interesting process for nanomaterial synthesis because it can produce high-purity nanocrystalline materials in one-step process, low operating cost, and suitable for large scale production of catalytic materials [2]. The aim of this research is to study the effect of Ti loading content in $Ru/Ti\text{-}SiO_2$ catalysts and $Ti\text{-}SiO_2$ supports prepared by using the FSP technique and the Ru deposition method on the physiochemical and catalytic properties of synthesized catalysts.

Experimental/methodology.

Synthesis of $Ru/Ti\text{-}SiO_2$ catalysts were carried out by one-step using flame spray pyrolysis and impregnation methods. The liquid feed solution was prepared by dissolving the desired amounts of all precursors in xylene. The precursor solution was fed to flame reactor as the conditions in our previous work [2]. In this work, the Ru deposition was done by directly added the Ru precursors in FSP solution and impregnation of Ru on FSP-made $Ti\text{-}SiO_2$ supports. Loading content of Ru was fixed at 2wt% and the Ti loading contents were varied from 2 to 12wt%.

Results and discussion.

Figure 1 plots between the CO_2 conversion and reaction temperatures of all prepared catalysts. In all tests, there was no CO formation in all catalysts. Among all catalysts, Ru/SiO_2 exhibited the lowest catalytic performance. Addition of Ti in Ru/SiO_2 catalysts resulted in the improvement of catalytic performance. In order to find the maximum Ti loading that can improve the catalytic activity, 12wt% of Ti was doping in FSP-made Ru/SiO_2 catalyst and $Ru/12Ti\text{-}SiO_2$ exhibited the highest CO_2 conversion. Moreover, deposition of Ru on $Ti\text{-}SiO_2$ support by impregnation method exhibited much higher catalytic performance than one-step FSP synthesized $Ru/Ti\text{-}SiO_2$ catalysts. After various physiochemical characterization of the catalysts, the FSP-maed catalysts exhibited very strong interaction between Ru and the supprt, which occurred by the coverage of SiO_2 particles around Ru species. This coverage was occurred due to the mix crystallization of both phase at nearly same time under the flame. This interaction prevent the reduction of RuO_2 phase to Ru activeside, which lower the the adsorption of CO_2 on the catalyts surface and catalytic activity of FSP-made catalysts. However, the impregnation-one can completely reduced and exhibited higher CO_2 catalytic performance. Addition of Ti also resulted the incrased of the catalytic activity in CO_2 methanation. Presence of TiO_2 phase promote the catalytic activity by increasing of Ru dispersion and retard the RuO_2 sintering during the high temperature process, which according to the increased of interaction between RuO_2 and TiO_2 species

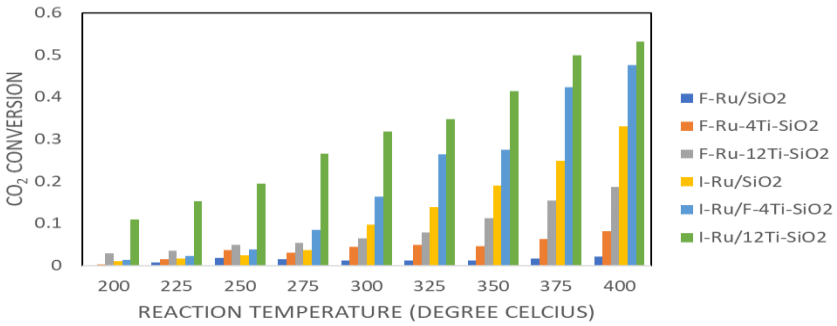

Figure 1 Plot between the CO2 conversion and reaction temperatures of all prepared catalysts**.**

Acknowledgments

The research has received funding support from the NSRF via the Program Management Unit for Human Resource & Institutional Development, Research and Innovation [grant number B1640034].

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Highly active, selective, and stable $CuZnAlO_x$ catalyst for methanol synthesis via CO_2 hydrogenation under industrially relevant conditions

H. Mena[1]*, N. Ortner[1], Dan Zhao[1], U. Armbruster[1], S. Wohlrab[1], E. Kondratenko[1]

[1]*Leibniz Institute for Catalysis, D-18059 Rostock, Germany*

**hesham.mena@catalysis.de*

Introduction:

The hydrogenation of CO_2 became one of the most promising routes not only to mitigate atmospheric CO_2 emissions but also to produce valuable single carbon (C1) products. Among them, methanol is a clean, biodegradable, high energy fuel, and can be further converted into value-added chemicals such as olefins, longer-chain alcohols and hydrocarbons [1]. Continuing our previous work [2], this study deals with improving methanol selectivity at industrially relevant degrees of CO_2 conversion [3] as a future part of a membrane reactor system for further enhancement of methanol productivity.

Experimental:

A series of CuZn-based catalysts were prepared and screened for CO_2 hydrogenation to methanol in a fixed-bed, continuous-flow stainless steel reactor under different reaction conditions. The feed gas and the reaction products were analyzed with an on-line gas chromatograph. The influence of reaction temperature, pressure, and feed gas composition on catalyst performance was studied. The most active $CuZnAlO_x$ catalyst was characterized by ICP, BET, XPS, TPR, TEM and XRD techniques.

Results and discussion:

Among the catalysts tested, a low-cost and ecologically friendly $CuZnAlO_x$ catalyst reached high methanol selectivity at industrially relevant CO_2 conversion. Figure 1 shows the CO_2 conversion and MeOH selectivity over 1900 h under different reaction conditions (T=180-250 °C, p=20 and 50 bar, H_2/CO_2=3, GHSV=280-4220 $ml_n\ g_{cat.}^{-1}\ h^{-1}$) . The highest methanol selectivity of about 93% was achieved at about 19% CO_2 conversion at 200 °C and 50 bar using a stoichiometric reaction feed. In repetitive measurements at a fixed set of reaction parameters (see figure 1, green circles), a slight asymptotic decrease in CO_2 conversion (16.0→13.5→12.9%) and in MeOH-selectivity (85.0→84.2→83.5%) was registered after 313 h and 1900 h on stream, respectively. Such capability to manage different reaction conditions is a basic requirement for catalysts to be combined with a membrane reactor, as temperature and concentration profiles change much more significantly along the reactor bed than in a classic tubular reactor. The presented catalyst is being tested for this application.

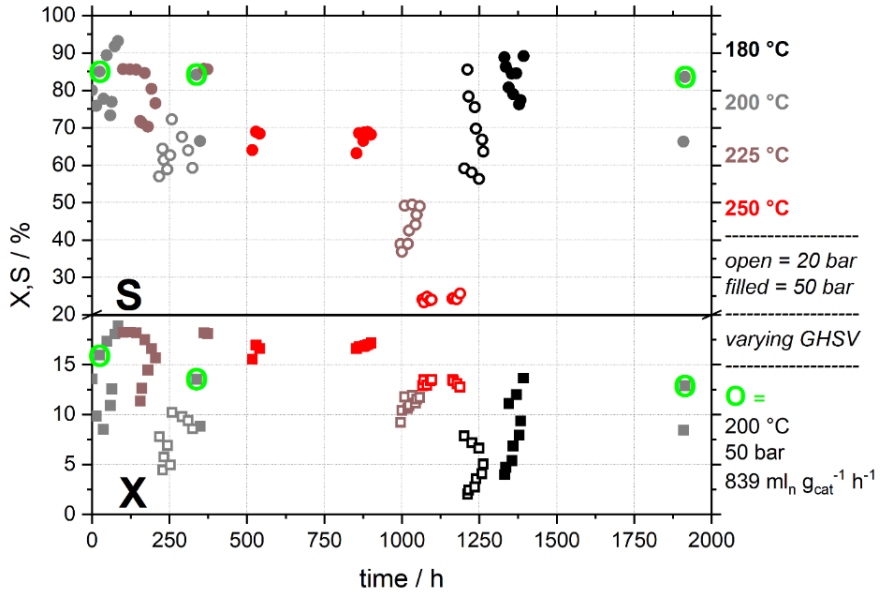

Figure 1. Long-term performance of $CuZnAlO_x$ in hydrogenation of CO_2 to methanol under different reaction conditions.

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CO_2 Capture and Utilisation by Using Switchable Dual Function Materials

Loukia-Pantzechroula Merkouri[1*], Tomas Ramirez-Reina[1,2], Melis S. Duyar[1]
[1]*School of Chemistry and Chemical Engineering, University of Surrey, Guildford GU2 7XH, UK*
[2]*Department of Inorganic Chemistry and Materials Sciences Institute, University of Seville-CSIC, 41092 Seville, Spain*
**Corresponding author: l.merkouri@surrey.ac.uk*

Keywords: CO_2 capture and utilisation, switchable dual function materials, heterogenous catalysis, CO_2 methanation, reverse water gas shift, dry reforming of methane, adsorption, direct air capture

Introduction. Global warming is increasing at an alarming rate and efforts, such as the Paris Agreement in 2015, are continuously made in an attempt to achieve net zero CO_2 emissions by 2050. To address the needs of energy transition, we have previously developed switchable catalysts for CO_2 utilisation, offering flexibility in production of methane, CO and syngas.[1] Herein we further extend this idea to the development of switchable dual function materials (DFMs).[2] DFMs capture CO_2 and convert it directly to a product, using hydrogen or hydrocarbons as co-reactants. They offer a unique opportunity to directly synthesise value added chemicals from sources of emissions, but also from the atmospheric air.[3]

Experimental/methodology. The three DFMs were prepared by impregnation and the materials were obtained from nitrates precursors. All the DFMs consisted of 15 wt.% of Ni, 1 wt.% of Ru, and 10 wt.% of either Na_2O, K_2O, or CaO supported onto CeO_2-Al_2O_3 (20-80 wt.%). Their CO_2 adsorption behaviour was investigated at 350-650°C by thermogravimetric analysis. H_2-TPR was performed to evaluate their reducibility and products were detected using a mass spectrometer. The feasibility study that included cycles of CO_2 capture and either CO_2 methanation, reverse water-gas shift (RWGS) or dry reforming of methane (DRM) were performed to observe their versatility. Time-resolved operando DRIFTS-MS studies were also employed to elucidate their capture and conversion mechanisms.

Results and discussion. Figures 1 reveals the feasibility of switchable DFMs, where 100% selectivity in conversion of captured CO_2 to either methane or CO is obtained for all 3 reactions (methanation, RWGS and DRM). In all cases, the CO_2 was captured at the desired temperature and was subsequently converted into CH_4, CO, and syngas, depending on the temperature and the co-reactant used. In terms of overall performance, DFMs can be ranked in the order NiRuCa>NiRuK>NiRuNa. A striking finding was the detection of CH_4 during this experiment during H_2-TPR (Figure 2), which demonstrated that these DFMs were able to adsorb CO_2 directly from atmospheric air after synthesis, showing the promise of using DFMs for flexible chemicals synthesis from the CO_2 in air.

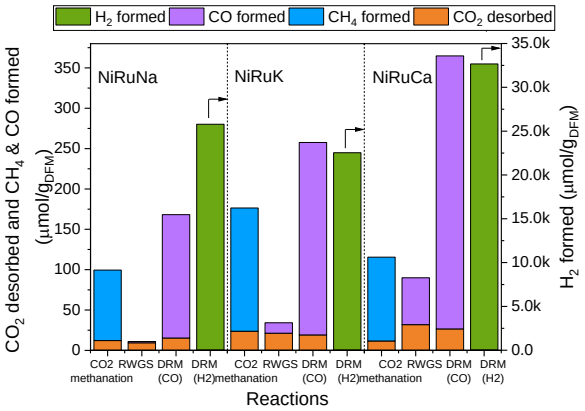

Figure 1. Results of feasibility study of flexible DFMs, showing the amount of CO_2 desorbed and products formation in each reaction (CO_2 methanation, RWGS and DRM) for NiRuNa, NiRuK and NiRuCa.

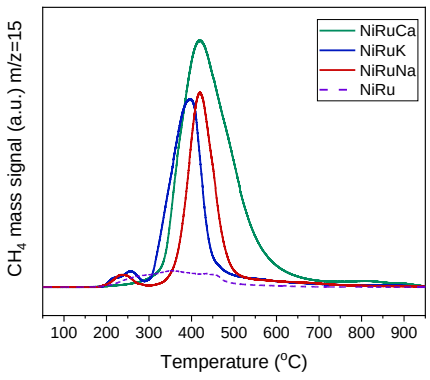

Figure 2. CH_4 signal during H_2-TPR with 10% H_2/Ar and 10 °C/min to 950 °C (WHSV= 60 $L.g^{-1}.h^{-1}$) for the three DFMs (NiRuNa, NiRuK and NiRuCa) and the reference material NiRu

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Nickel embedded silica catalyst for highly stable performance of dry reforming of methane (DRM)

Haehyun Min[1], Young Jin Kim[2] and Sung Bong Kang[1*]

[1] *Gwangju Institute of Science and Technology, Gwangju, Republic of Korea*
[2]*Korea Research Institute of Chemical Technology, Daejeon, Republic of Korea*
[*]*sbkang@gist.ac.kr*

Introduction.

The catalytic reaction of the dry reforming of methane (DRM, $CO_2 + CH_4 \rightarrow 2H_2 + 2CO$) has been extensively receiving more attention to actively address tremendous emissions of greenhouse gases (CO_2 and CH_4) converting to syngas (H_2 and CO) [1]. However, the catalyst deactivation by metal sintering and carbon coking is a significant issue in applying DRM to a chemical process. Here, we report a highly active catalyst in the DRM reaction; Ni embedded in silica structure (NiES), demonstrating long-term stability up to 500 hrs of time-on-stream under high flow rate conditions up to 450 $Lg_{cat}^{-1}h^{-1}$.

Experimental/methodology.

The NiES catalyst was prepared by (1) introducing a certain amount of a Ni precursor into the amine-functionalized silica by introducing oleic acid and uniformly mixing it with the silica and (2) subsequently adding the Ni precursor to the mixture (1) obtaining a final loading of 10 wt.% Ni. The final mixture was calcined at 800 °C for 2 hrs after drying at 80 °C. The catalytic performance was evaluated under a feed containing 0.3:0.3:0.4 of CH_4:CO_2:Ar ratio at 250-450 $Lg_{cat}^{-1}h^{-1}$ of GHSV.

Results and discussion.

Figure 1a shows an outstanding performance of the NiES catalyst, of which 98% and 97% of CO_2 and CH_4 conversions and a stoichiometric H_2/CO ratio, respectively, at 800 °C, without any degradation. Furthermore, we have demonstrated that (1) NiES consists of only active metals and supports without promoters, (2) is prepared in a feasible method that all steps are performed in one pot, and (3) has excellent catalytic activity and durability at high space velocities (as compared in Figure 1b). These activity results were confirmed by detailed studies and controlled experiments, and the outstanding catalytic activity was derived from the catalyst structure. Highly dispersed nano-sized (2 nm, Figure 1c and d) Ni particles are phyllosilicate-like forms that are embedded in silica structures preventing sintering due to the confinement effect. The formation of Ni-O-Si interaction by phyllosilicate-like forms enhanced properties such as reducibility and surface acidity of the catalyst, and these properties greatly contributed to the mechanism of DRM. Based on the vital intermediates identified by the DRIFT spectra the mechanism over the NiES surface was proposed.

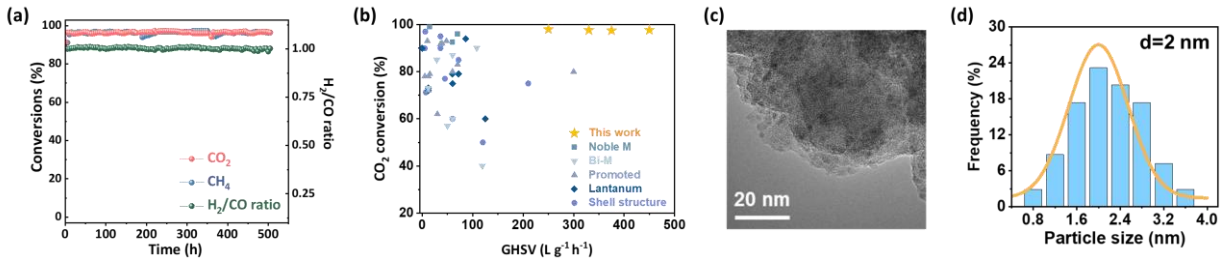

Figure 1 (a) Long-term stability of the NiES at 800 °C with a flow of 250 $Lg_{cat}^{-1}h^{-1}$, (b) Comparison of catalytic performance of NiES with literature reports as a function of GHSV, (c) TEM image of NiES and (d) Size distribution of Ni particles.

Acknowledgments

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Investigating the effect of nickel loading on Ni/CeO_2-nanorods for plasma-catalytic CO_2 methanation

J. Barauna[1*], B. Musig[1], T. Garcia[1], M.V. Navarro[1,]

[1] *Grupo de Investigaciones Medioambientales, Instituto de Carboquímica ICB-CSIC, Zaragoza, Spain*

[*] *joliveira@icb.csic.es*

Keywords: CO2 methanation, plasma catalysis, single atom catalyst

Introduction: CO2 valorization is a crucial research area for reducing greenhouse gas emissions and tackling climate change. In that context, plasma-assisted catalysis is a promising technique for synthesizing valuable compounds from CO2, using the unique characteristics of plasma, coupled with the tuning effects of catalysts to improve selectivity and conversion. It is well known that the amount of active phase on a catalyst affects its performance, but in the particular case of plasma-catalysis this may differ due to the mutual influence of catalyst composition and plasma. This happens due to strong electric fields, surface charging, hot spot formation, and morphological changes of the catalyst [1]. Also, active phases and supports have great mismatch in electric conductivity, heat capacity and other important properties and these have an effect on the plasma [2]. Ni-based catalysts and CeO2 supports are commonly used in CO2 methanation, with nanostructured CeO2 being particularly effective due to its excellent redox properties and ability to adsorb and desorb oxygen [3] while Ni is commonly employed in thermal CO2 methanation due to its favorable selectivity and performance, low cost and ability to perform well even in mild conditions

Materials and methods: In this study, CeO2 nanorod supports were impregnated with three different loadings of Nickel and tested in the CO2 methanation using a packed-bed dielectric barrier discharge (PB-DBD) reactor. The nanorods were synthesized hydrothermally and then wet impregnated with 5%, 10%, 15%wt. Ni, calcined in air at 550°C and reduced in 5% H 2 at 600°C for 2 hours. The catalysts were characterized, before and after the discharge, using XRD, XPS, H_2-TPR, CO_2-TPD, TGA and N_2 physisorption.

Results and discussion: results show that the nanorods retain its shape after the reduction of Nickel and the dispersion of the active phase is greatly impacted by the loading. While samples containing 5% nickel were populated by uniform small Ni particles, 15% %wt. Ni results in larger particles with a great distribution of sizes. Nevertheless, plasma exposure can change the dispersion of the active phase and larger Ni particles can be reduced in size and redistributed, as it is reported for plasma-treat catalysts [ref]. This reflected in the results, and the best performing catalyst was the one with 15% nickel (82% CO_2 conversion and selectivity to methane close to 100%), since plasma during the reaction was effective in redistributing the nickel over the support, allowing it to benefit from the higher amount of active-phase. We can then conclude that while some similarities with other types of catalysis can hold, plasma-catalysis has unique features that can change paradigms and greatly affect the performance of CO_2 methanation.

Acknowledgments: The authors would like to thank MSCA ITN grant N° 813393 and the Departamento de Ciencia, Universidad y Sociedad del Conociemiento del Gobierno de Aragón for Project LMP151_21.

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Design and development of a thermo-photo catalytic system to boost the activation of small molecules by plasmonic effect

G. Miroddi[1], M. Boaro[1*], A. Trovarelli[1]

[1]Dipartimento Politecnico, Università degli Studi di Udine, 33100 Udine, Italy.

[*]*marta.boaro@uniud.it*

Keywords: CO_2 reduction, Thermo-photo catalysis, Local Surface Plasmon Resonance (LSPR) , Methane

Introduction. CO_2 capture and valorization[1] as a climate change mitigation measure has recently attracted the scientific community interest.[1] In catalysis, many strategies have been studied to reach the goal. One of the most recent and potentially winning strategies is to use a combination of heat and light to maximize the activity of catalysts towards carbon dioxide reduction.[2] Light would minimize the thermal energy supply and improve selectivity stimulating the LSPR phenomenon of metal catalysts nanoparticles (Au, Rh, Cu)[3,4] The aim of this work is to deeply investigate this phenomenon in Sabatier reaction over Rhodium-supported Cerium-Titanium Mixed Oxides, chosen for the well-known plasmonic effect of Rh[5], and the interesting surface arrangements attained with CeO_2-TiO_2 solid oxide solutions[6], which have a positive role in CO_2 activation[7].

Experimental. Different Cerium-titanium mixed oxide compositions (X mol%CeO_2: (1-X) mol%TiO_2, X=100, 80, 50, 20) where prepared by Sol-Gel route. Rhodium was added by incipient wet (IW) impregnation of Rh-acetate or by ball milling (BM) the rhodium salt and the oxides. The final supported catalysts were calcined at 500°C and reduced in situ in H_2 before testing. Physico-chemical properties of materials were investigated with XRD, BET-porosimetry, H_2-TPR, SEM-EDS techniques. LSPR response of the different catalysts and the their thermo-photocatalytic activity (CO_2 conversion, CH_4 yield) were investigated in presence and absence of light using a 300W Xenon lamp light source.

Results and discussion. The LSPR effect of metal nanoparticles was confirmed by a 3% increase in temperature that was registered for the Rh-supported catalysts in comparison to bare supports upon illumination under inert atmosphere. The better catalytic performances were obtained for BM catalysts, with an optimum for the composition 80mol%CeO_2-20mol%TiO_2. This formulation showed a 19% enhancement in conversion and almost 100% selectivity in light condition at 300°C with respect to the dark test. Fig. 1 shows that light in general is beneficial in improving the selectivity of reaction. Studies are in progress to understand the role of structure and composition of support in optimizing a significant LSPR effect at lower temperature.

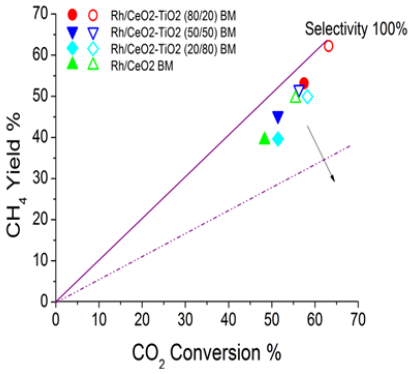

Fig. 1 Yield-Conversion - plot at 300°C isotherm. Solid and empty symbols represent dark and light experimental condition respectively; 33 ml/min gas mixture 28% He / 61% H_2 /11% CO_2.

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Modified ferrites for the magnetically heated CO_2 reduction

J. Moral-Pombo[1], S. Ghosh[2], B. Chaudret[2] , A. Belén Dongil[1], E. García-Bordejé[3], I. Rodríguez-Ramos[1*]

[1]*Instituto de Catálisis y Petroleoquímica (CSIC), Madrid, Spain*

[2]*Laboratoire de Physique et Chimie des Nano-Objets (CNRS), Toulouse, France*

[3]*Instituto de Carboquímica (CSIC), Zaragoza, Spain*

[*]*irodriguez@icp.csic.es*

Introduction. Decreasing anthropogenic CO_2 emissions is compulsory to mitigate the problematic effects of global warming. In that sense, shifting the paradigm from a linear carbon economy to a circular one is a good step in this direction. [1] The Sabatier and the Reverse Water Gas Shift reactions are paradigmatic examples of this strategy. [2] Nonetheless, they imply the need for a catalyst due to the stability of the CO_2 molecule. Being so, magnetic induction heating or "magnetically-assisted catalysis" is an already proven feasible technique that helps achieve the required temperature at the active centres using an external magnetic field. This avoids undesired secondary reactions and increases the efficiency of the process while heating and cooling velocity are drastically improved. [3] Under this context, the chemical storage of energy from renewable intermittent sources would be facilitated. In this work, nickel and cobalt ferrites have been synthesized and studied as bifunctional materials. They combine a catalytic activity for CO_2 reduction to CO and CH_4 and the necessary heating ability for magnetically-assisted catalysis.

Experimental/methodology. Nickel ($NiFe_2O_4$) and cobalt ($CoFe_2O_4$) ferrites were synthesized using different synthesis methods: autocombustion sol-gel, Pechini and template-directed approach employing a MOF (Fe-BTC). Afterwards, 2.3%Ni/$CoFe_2O_4$ and 4%Ru/$CoFe_2O_4$ were obtained through impregnation. The materials' heating ability was studied by evaluating the required field intensity to reach the reaction temperature in the magnetically-assisted catalytic reactor. Magnetic methanation was performed using a glass tubular reactor that was placed inside a 100 kHz coil. The catalytic bed was composed of the selected ferrite and SiC. Gases from the outlet were quantified by gas chromatography. Finally, ferrites were characterized by X-ray Diffraction, BET area, vibrating sample magnetometry and temperature programmed reduction.

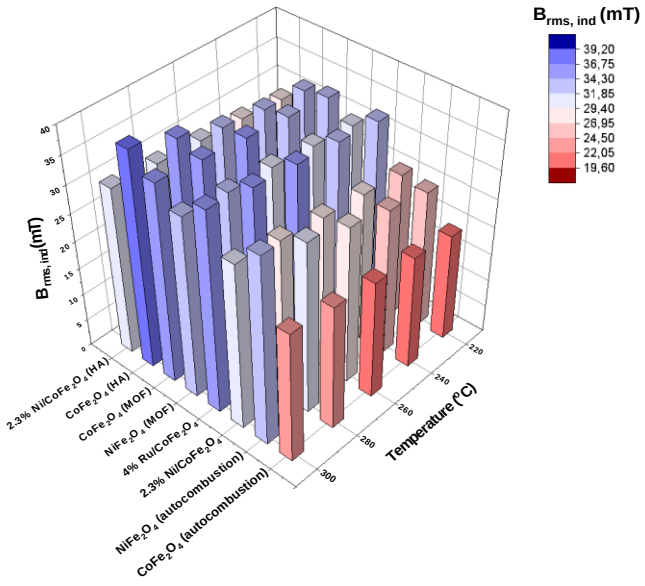

Figure 1. **Required magnetic field intensity to reach the reaction temperatures for each ferrite.**

Results and discussion.

a. Heating ability of the ferrites. $CoFe_2O_4$ (sol-gel) results in the most promising heating agent for magnetically-assisted methanation. Ni-Fe and Co-Fe alloys are formed during the pretreatment of the catalyst, specially in the case of $CoFe_2O_4$.

b. Methanation tests. Low to moderate conversions were achieved. $CoFe_2O_4$ (sol-gel) is extremely selective for the production of CO ($S_{CO,\ 300\ ºC}$ = 95%), while showing moderate conversions ($X_{CO2,300\ ºC}$ = 60%). Regardless of the synthesis method, $NiFe_2O_4$ exhibits a higher s_{CH4}, but lower conversions. Increasing the surface area of $CoFe_2O_4$ and impregnating active metals like Ni also result in higher S_{CH4}.

c. Characterization. H_2 consumption peaks were identified and assigned. Magnetization curves were obtained. The materials are soft ferrimagnets with higher saturation values than those reported on the literature. Differences in synthesis method translate into different BET areas.

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Synergy of single-atom Ni and Ru on CeO_2 catalysts for plasma-assisted CO_2 methanation

B. Musig[1,2], J. Barauna[1], T. Garcia[1], M. E. Galvez[2], M. V. Navarro[1,*]

[1] *Grupo de Investigaciones Medioambientales, Instituto de Carboquímica ICB-CSIC, Zaragoza, Spain*

[2] *Institut Jean le Rond d'Alembert, CNRS UMR 7190, Sorbonne Université, Paris, France*

[*] *navarro@icb.csic.es*

Keywords: CO2 methanation, plasma catalysis, single atom catalyst

Introduction. CO_2 valorisation is one of the players for the de-fossilization of energy production and industrial manufacturing, it comprises of different strategies of CO_2 capture and utilization (CCU) [1] and it requires fundamental research and engineering to efficiently break the CO_2 molecule and have it react to form added-value chemicals. One of the possible reactions is the reduction of CO_2 to methane, a.k.a. Sabatier's reaction. This reaction between CO_2 and H_2 has been widely studied in conventional catalysis: it is known to be exothermic but kinetically hindered, therefore happening with the aid of a catalyst typically between 200 °C and 450 °C, at pressures between atmospheric and 100 bar [2]. The use of non-thermal plasmas is promising for energy efficient CO_2 conversion exploiting the dissociation happening in plasma via electron impact and vibrational excitation. Additionally, the synergy between the plasma and the catalytic material can further enhance the reaction performance, as it has been demonstrated for Ni-containing catalysts resulting in an enhanced reaction yield even at atmospheric pressure and mild reaction temperatures (around 200 °C) [3].

Ru and Ir on CeO_2 single-atom catalysts have been previously used for thermal CO_2 methanation, reporting effects on strong metal-support interaction, metal dispersion, cerium oxide crystalline structure and hydrogen spill over that affect differently the catalyst activity and CH_4 selectivity [4,5].

Experimental/methodology. A one-pot hydrothermal method was used for the synthesis of Ni-Ru single atom $Ni_xRu_yCe_{(1-x-y)}O_2$ materials with x = 0.05, 0.025, 0 and y = 0, 0.025, and 0.05. The relative metal salts were dissolved in a 6 M NaOH solution, poured in an autoclave and placed in an oven at 120 °C for 24 h. The material recovered via filtration was dried, calcined at 400 °C, and reduced before the reaction [6]. The catalysts were characterized by means of XRD, N_2 physisorption, XPS, H_2-TPR, CO_2-TPD, and TEM. Plasma-assisted CO_2 methanation was carried out in a non-thermal Dielectric Barrier Discharge (DBD) plasma reactor. The high voltage electrode of the cylindrical DBD fixed-bed reactor was supplied by a high-voltage, alternating current source with frequency 27 kHz and voltage 20-25 kV.

Results and discussion. The morphology of the doped ceria structures is needle-like and the crystallite size of the cerianite phase does not vary drastically with the introduction of the metal sites from 7 to 9 nm. Regarding the physicochemical properties of the single-atom catalysts, we report that for low %mol. Ni and Ru clusters are well dispersed in the ceria crystalline structure as the diffraction peaks are not detectable in XRD [6]. Furthermore, the reducibility of the materials is improved at low temperatures compared to Ni/CeO_2 materials obtained via wet impregnation. The low amount of metal sites does not allow reaching a high activity for plasma-assisted CO_2 methanation compared to previous tests carried out with 15 %wt. Ni catalysts; however, it is still relevant if normalized by mol_{metal}. The catalyst with both Ni and Ru sites, $Ni_{0.025}Ru_{0.025}Ce_{0.95}O_2$, results in an enhanced CO_2 conversion, indicating synergy between the two metals in the catalytic methanation reaction assisted with plasma.

Acknowledgments: *The authors would like to thank MSCA ITN grant N° 813393 and the Departamento de Ciencia, Universidad y Sociedad del Conocimiento del Gobierno de Aragón for Project LMP151_21.*

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Low-temperature hydrogenation of CO_2 to methanol over supported gold catalysts

Takumi Nakagawa[1], Hiroki Miura[1,2,3], Tetsuya Shishido[1,2,3*]

[1]*Tokyo Metropolitan University. Tokyo, Japan*
[2]*Research Center for Hydrogen Energy-Based Society, Tokyo Metropolitan University. Tokyo, Japan*
[3]*Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Kyoto, Japan*
**shishido-tetsuya@tmu.ac.jp*

Keywords: Supported Au catalysts, CO_2 hydrogenation, Methanol

Introduction.

Catalytic conversion of CO_2 to value-added chemicals using green H_2 derived from renewable energy is essential to develop a carbon-neutral society[1]. Among CO_2 hydrogenation products, methanol (CH_3OH) as a primary chemical has attracted much attention. Recently, direct CH_3OH synthesis from CO_2/H_2 has been developed using Cu-based catalysts. This reaction is exothermic; therefore, the lower temperature is thermodynamically more favorable. In this study, various metal oxides-supported Au catalysts were prepared, and the activity for CO_2 hydrogenation at low temperatures (< 473 K) was investigated.

Experimental/methodology.

Supported Au catalysts were prepared by the deposition-precipitation with urea[2]. Catalytic tests were carried out in a fixed-bed flow reactor. The diameter of Au was estimated by HAADF-TEM.

Results and discussion.

The catalytic performance of various supported Au catalysts was evaluated in CO_2 hydrogenation at 473 K. Among the Au catalysts tested, Au/ZrO_2 showed the highest CH_3OH formation rate. However, CO was mainly formed. Au/ZnO exhibited the highest CH_3OH selectivity (75%) without unfavoured CH_4 formation.

Fig.1 shows the turnover frequencies (TOFs) for the formation of CH_3OH at 473 K as a function of the mean diameter of Au NPs on supported Au catalysts. To determine whether the active sites for the CO_2 hydrogenation to CH_3OH were exposed Au atoms on the Au NPs or perimeter sites at the Au-support interfacial perimeter, we calculated the TOFs in two ways: 1) by normalizing the number of CH_3OH molecules formed per hour to the total number of exposed Au atoms at the Au NPs (TOF-S) and 2) by normalizing the number of CH_3OH molecules formed per hour to the total number of Au atoms at the Au-support interfacial perimeter (TOF-P). TOF-S decreased with increasing mean Au NPs diameter, whereas TOF-P remained nearly constant. These results suggest that the active sites for CO_2 hydrogenation to CH_3OH are the Au-support interfacial perimeter, and CH_3OH is generated by the reaction between CO_2 adsorbed on the Au-support interface and H_2 dissociatively adsorbed on the Au NPs.

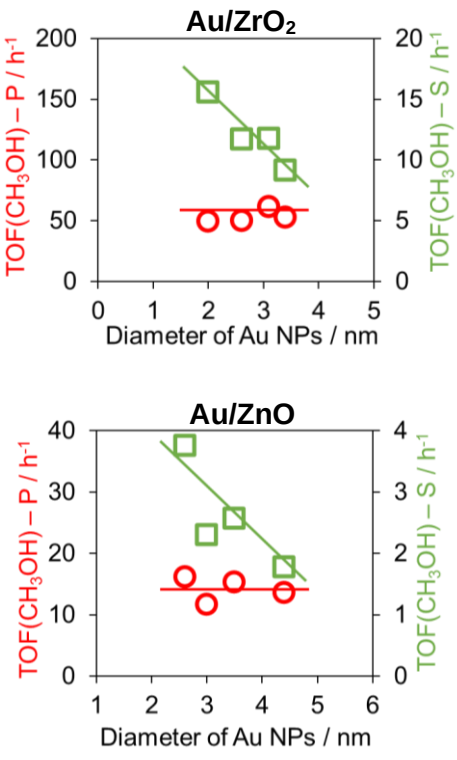

Fig.1 Relationship between diameter of Au NPs and TOF-P (○) and TOF-S (□) for CH_3OH formation.
Pretreatment: H_2 reduction at 473 K
Reaction: 473 K, CO_2/H_2 = 1/3, 4 MPa

Acknowledgments

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Lecture / Elucidating CO_2 methanation mechanism over novel 10% $LaNiO_3/CeO_2$-derived catalyst by in-situ FTIR and NAP-XPS

Jon A. Onrubia-Calvo[1*], S. López-Rodríguez[2], Ignacio J. Villar-García[3], Virginia Pérez-Dieste[3], A. Bueno-López[2], Juan R. González-Velasco[1]

[1]Dept. of Chemical Engineering, Faculty of Science and Technology, Universidad del País Vasco UPV/EHU, Barrio Sarriena, s/n, 48940 Leioa, Bizkaia, Spain
[2]Dept. of Inorganic Chemistry, University of Alicante, C. San Vicente del Raspeig s/n, E-03080 Alicante, Spain
[3]ALBA Synchrotron Light Source, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallès, Barcelona, Spain
[*]jonander.onrubia@ehu.eus

Introduction. CO_2 hydrogenation is a hot topic, being a relevant step to satisfy future energy demand and supply building blocks for the petrochemical industry while mitigating CO_2 emissions. 10% $LaNiO_3/CeO_2$ formulation has emerged as a promising precursor of highly active, selective and estable catalysts for CO_2 methanation [1]. However, the role of the active sites and the main reaction intermediates is still unclear. The aim of the current study is to monitor the behavior of the different Ni, La and Ce species as well as reaction intermediates during CO_2 methanation reaction using NAP-XPS and in-stu FTIR techniques.
Experimental/methodology. The surface of the sample, prepared as reported elsewhere [1], has been monitored during the exposure to pure H_2, pure CO_2 and CO_2 methanation (20% CO_2 + 80% H_2) atmospheres at increasing temperatures by Near Ambient Pressure-XPS (NAP-XPS) using synchrotron radiation at the CIRCE beamline, ALBA Synchrotron Light Source. Ni3p, Ce3d, La3d and C1s regions were monitored with 320, 375 and 1125 eV photon energies. Meanwhile, the role of the different active sites and reaction intermediates in the CO_2 methanation mechanism was evaluated by *In-situ* FTIR anlaysis. For that, a Cary 600 Series FTIR spectrometer (Agilent) coupled with a high temperature cell equipped with ZnSe windows (Specac) was used.
Results and discussion. After subjecting the 10% $LaNiO_3/CeO_2$ sample to controlled reduction step (500 °C), small Ni^0 nanoparticles and a La_2O_3 phase in close contact with ceria support are conformed. As a result of these strong interactions, a certain proportion of nickel always remains oxidized under reaction conditions. Among them, the species involved in the redox processes taking place during the CO_2 methanation mechanism are the Ni^{2+}-CeO_2/Ni^0 and Ce^{4+}/Ce^{3+} pairs, which tend to be oxidized under CO_2 methanation conditions at increasing temperatures.
In-situ FTIR experiments allow indetifying the participation of formates, bicarbonates as well as mono-, bi-dentate carbonates intermediates during CO_2 methanation (Figure 1). It is worth to mention that formate intermediate disappears as long as CH_4 production increases, in line with the identification of the formate peaks made in the C1s region during NAP-XPS experiments. Thus, the formate route, with assistance of the oxygen vacancy of ceria support and La_2O_3 basic sites, is expected as the most feasible mechanism for CO_2 methanation over this novel material. Based on these results, the high activity of the 10% $LaNiO_3/CeO_2$–derived catalyst is tentatively attributed to the simultaneous presence of Ni^{2+}-La_2O_3, Ni^{2+}-CeO_2 and Ni^0 active sites, where CO_2 and H_2 can be associatively and dissociatively adsorbed, respectively.

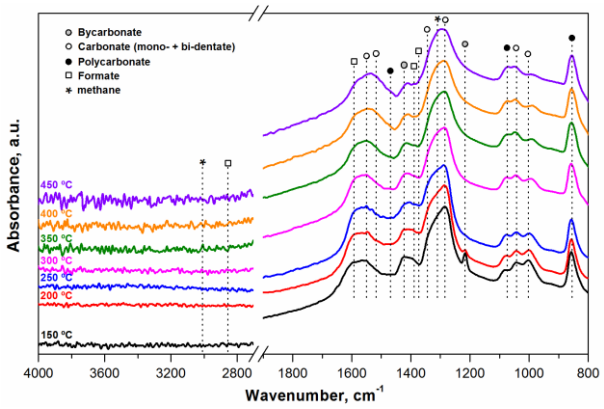

Figure 1. *In-situ* FTIR spectra for the pre-reduced 10% $LaNiO_3/CeO_2$ sample during CO_2 methanation at different temperatures.

Acknowledgments
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Enhancement the CO_2 adsorption and hydrogenation to CH_4 capacity of Ru-Na-Ca/γ-Al_2O_3 dual function material by controlling the structure under different calcination atmosphere

A. Bermejo-López, B. Pereda-Ayo., J. A. Onrubia-Calvo, J. A. González-Marcos, J. R. González-Velasco*

Department of Chemical Engineering, Faculty of Science and Technology, Universidad del País Vasco UPV/EHU, Barrio Sarriena, s/n, 48940 Leioa, Bizkaia, Spain
**Corresponding Author's E-mail address: juanra.gonzalezvelasco@ehu.eus*

Keywords: integrated CO_2 capture and utilization, methanation, dual function material, calcination atmosphere.

Introduction. Integrated CO_2 capture and utilization (ICCU) technology requires the implementation of dual function materials (DFMs) to carry out the process in a single reaction system[1]. In this work, the possibility of improving the activity of a previously optimised DFM formulation[2] (4% Ru-8%Na_2CO_3-8%CaO/γ-Al_2O_3) by modifying the calcination atmosphere is studied.

Experimental. A single batch of DFM was prepared by sequential wetness impregnation, which was splitted into four alliquotes. One of them was calcined in static air inside a muffle (RuNaCa-air), whereas the remaining three were calcined in a horizontal furnace under different gas mixtures. Two of them under reducing atmosphere (RuNaCa-10H_2 and RuNaCa-50H_2) and the last one in an inert atmosphere (RuNaCa-N_2). The four DFMs were deeply characterized by XRD, TG, N_2 adsorption-desorption, H_2 chemisorption, TEM, H_2-TPD, H_2-TPR, CO_2-TPD and TPSR. The catalytic behavior was evaluated, in cycles of CO_2 adsorption and hydrogenation to CH_4, and the temporal evolution of the concentration of reactants and products was analyzed.

Results and discussion. DFMs with high metallic dispersion are obtained in all cases, and it was confirmed that the reduction pretreatment prior to the activity tests reduced completly the ruthenium phase. The calcination atmosphere did not alter significantly the basicity of the DFMs; however, a stronger effect on the reactivity of the adsorbed CO_2 was identified for the samples prepared under different calcination atmosphere. In the TPSR experiments, RuNaCa-N_2 and RuNaCa-air DFMs produced a significantly higher amount of CH_4. It is proposed that the DFMs calcined ubder an inert flow and muffle have a better arrangement between the adsorbed carbonates and the metal sites; in fact, they present the highest surface area values, especially DFM RuNaCa-N_2 (134 m^2 g^{-1}).

Figure 1 shows the catalytic activity in CO_2 adsorption and hydrogenation to CH_4 sucessive cycles. For all DFMs the same general trend is observed. Note that the formulation of the four DFMs is the same and only the calcination atmosphere is varied. However, differences in production of CH_4 (Y_{CH4}) can be observed. RuNaCa-N_2 DFM presents the highest Y_{CH4}=449 µmol g^{-1} at 370 °C. Therefore, it is concluded that calcination atmosphere significantly influences the physico-chemical properties and, consequently, the activity of each DFM. The DFM RuNaCa-N_2 is proposed as the optimum of this study; and therefore, calcination in flow of N_2 is selected as optimal for presenting the best arrangement conformed between ruthenium and the adsorbent phases to enhance activity in ICCU.

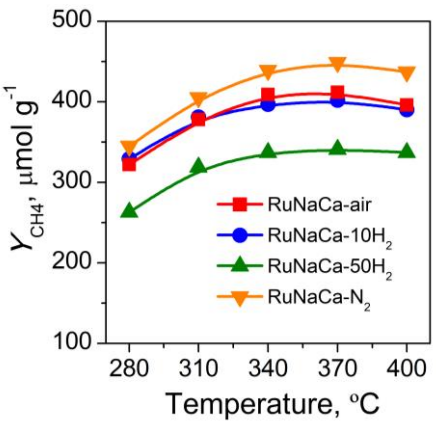

Figure 1. Evolution of CH_4 productions with operating temperature for the DFMs.

Acknowledgments
Support for this study was provided by Project PID2019-105960RB-C21 by MCIN/AEI/10.13039/501100011033 and the Basque Government (Project IT1509-2022).

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CO_2 Hydrogenation to Renewable Methane on Ni/Ru Modified ZSM-5 Zeolites

M. Oykova[1]*, M. Popova[1], M. Dimitrov[1], D. Karashanova[2], D. Kovacheva[3], G. Atanasova[3], Á. Szegedi[4]

[1] *Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria;*

[2] *Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Sofia, Bulgaria;*

[3] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria;*

[4] *Research Centre for Natural Sciences, Institute of Materials and Environmental Chemistry, Budapest, Hungary*

[*] *Corresponding Author's E-mail address: manuela.oykova@orgchm.bas.bg*

Keywords: ZSM-5 zeolite; bifunctional catalysts; renewable methane production; gas phase reaction

Introduction. The ongoing intensive use of conventional fuels is associated with increasing carbon emissions and their serious impact on the climate. The European Green Deal, as part of the EU's long-term strategy, aims to address climate change issues by eliminating net greenhouse gas emissions by 2050, most notably CO_2, whose emissions reach a record amount of 420 ppm in 2020 [1]. In recent years, technologies have been developed and industrialized to capture CO_2 from outgoing gas streams or directly from the atmosphere, after which it can be utilized via transformation processes to chemical substances and fuels [2]. This can be achieved by carboxylation reactions, where the CO_2 molecule is used as a precursor for organic compounds, such as carbonates, acrylates and polymers, or in reduction reactions to produce methane, methanol, synthesis gas, urea or formic acid [3].

In this study, template-free micro-mesoporous ZSM-5 zeolite was synthesized and modified with Ni and/or Ru. The obtained catalysts were investigated in the CO_2 hydrogenation to renewable methane.

Experimental. The obtained materials were characterized by X-ray powder diffraction, N_2 physisorption, temperature-programmed reduction (TPR-TGA), TEM and XPS spectroscopy. Hydrogenation of methane was studied at an atmospheric pressure using a fixed-bed flow reactor in the temperature range 250–400 °C with a flow rate of 90 mL/min H_2, CO_2 and N_2 (50%) (H_2/CO_2 is 4/1).

Results and discussion. Mono- and bimetallic Ni- and Ru-modified micro-mesoporous ZSM-5 catalysts were prepared by wet impregnation. Formation of finely dispersed nickel and/or ruthenium oxide species was observed on the external surface and in the pores of zeolite support. It was found that the peculiarity of the used zeolite structure and the modification procedure determine the type of formed metal oxides, their dispersion and reducibility. The applied Ni content, the addition of Ru as a second metal and the sequence of the modification by two metals are of key importance for the preparation of bimetallic catalysts with appropriate physico-chemical characteristics. XPS study revealed that the surface became rich in nickel and poorer in ruthenium for bimetallic catalysts. However, surface density of ruthenium is lower in bimetallic preparations compared to the monometallic one. TPR study confirmed the facilitated reducibility of nickel oxide particles in the presence of noble metal. Among the studied catalysts, 10Ni5Ru/ZSM-5 composition shows the highest activity and high selectivity for methane formation, reaching the equilibrium conversion and 100% selectivity at 400 °C. High stability and good reusability were found for the bimetallic 10Ni5Ru/ZSM-5 catalyst.

Acknowledgments

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ZrO_2 effect in the activity of Cu/CeO_2 catalysts for the reverse water gas shift reaction

M. Palma[1*], N. Barrabés[2], M. Sanchez-Sanchez[1]

[1] *Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, Getreidemarkt 9/166, Vienna 1060, Austria*

[2]*Institute of Materials Chemistry, TU Wien, Getreidemarkt 9/165, Vienna 1060, Austria.*

[*]*Corresponding Author: mireia.palma@tuwien.ac.at*

Keywords: reverse water-gas-shift, Cerium Oxide, Copper, CO_2 utilization, Zirconium Oxide

Introduction

Reverse water gas shift (RWGS) have received recently attention as a way to utilize CO_2 to produce syngas. Among RWGS catalysts, inexpensive Cu-based materials are of interest because they have shown high activity and selectivity .[1] However, it has also been demonstrated that the nature of the support can affect the catalytic performance. In particular, reducible oxides are regarded as good supports for RWGS, because their reducible properties can be modulated to improve the catalytic performance.[1] CeO_2 as catalyst support has been used to investigate the RWGS reaction because of its ability to form oxygen vacancies and its oxygen storage and release capacity, which have been demonstrated to assist in the conversion of CO_2 to CO.[2, 3] ZrO_2 is known to enhance oxygen mobility when added to CeO_2. [4] In this work we study the effect of adding adding ZrO_2 on the activity in RWGS of Cu/CeO_2 catalysts with different metal loadings.

Experimental

The CeO_2-ZrO_2 supports have been synthetized by co-precipitation, with loadings of ZrO_2 between 15%wt to 50%wt. The Cu was then introduced in a range of loadings between 5%wt and 28%wt by impregnation of the supports with Cu nitrate solutions, followed by calcination at 500°C for 4 hours. Activity tests were performed in a 3 mm diameter quarz reactor, after reduction of the catalyst at 300°C to generate Cu particles, at differential conditions in the lower temperature range (250°C to 350°C) in order to obtain the kinetics parameters. The gases were analyzed by gas chromatography.

The characterization of the catalysts have been performed by XRD and X-ray absorption spectroscopy, as well as temperature-programmed reduction.

Results and discussion

The results show that among the catalysts tested, Cu supported on CeO_2 has the highest activity at the 250°C - 350°C temperature range. On the other hand, the apparent energy of activation was similar for all the materials studied, indicating same reaction mechanism for all the catalyst formulations tested. The addition of ZrO_2 to CeO_2 achieved and increase in the CO yields, while carbon deposition is detected for the CeO_2 support. The characterization of these catalysts shows an increase in the Cu particle size upon reduction when CeO_2 is used as support. In contrast, ZrO_2CeO_2 supports stabilize Cu particles in sizes of ca. 30 nm. Further studies on the CeO_2ZrO_2 support will lead to insights on the role of support on the activity of Cu particles for RWGS.

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Hydrogen Production from Chemical Looping Reforming of Methane: a screening of Ni based Oxygen Carriers

L. Consentino[1,2], F. Deganello[2], R.Guil-Lopez[3], G. Pantaleo[2*], L. F. Liotta[2], R.M. Navarro[3], V. La Parola[2]

[1] *Department of Biological, Chemical and Pharmaceutical Sciences and Technologies (STEBICEF), University of Palermo, V.le delle Scienze Ed. 17, 90128 Palermo, Italy;* [2] *Institute for NanoStructured Materials, Italian National Research Council (ISMN-CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy,* [3] *Instituto de Catálisis y Petroleoquímica, Spanish National Research Council (ICP-CSIC), 28049 Madrid, Spain*

[*] *giuseppe-pantaleo@cnr.it*

Keywords: Hydrogen Production,Chemical looping Technologies, Nickel based mixed oxides, like-hydrotalcites materials

Introduction. Hydrogen is an energy vector with attractive attributes, such as lightness, storability, reactivity, high energy content per unit mass, and ease production on industrial scale. Furthermore, hydrogen can be used without direct emissions of air pollutants or greenhouse gases and can be produced from a diverse range of low-carbon energy sources. Chemical looping technologies can be used as a valuable approach for hydrogen production, due to the high energy efficiency and inherent CO_2 capture ability[1]. This study deals with the investigation of five type of nickel- based oxygen carrier materials active in methane reforming for hydrogen production through chemical looping technologies.

Experimental/methodology. Five catalysts with Nickel in different environments were prepared: Nickel supported on Ceria (**Ni/Ce**), Ni coprecipitated with cerium oxide (**NiCe**), **NiAlMg** or **NiAlCa** mixed oxide prepared by like-hidrotalcites materials, thermal decomposition and Ni in **$LaNi_{0.8}Co_{0.2}O_3$** perovskites structure. All samples were characterized by X-ray diffraction (XRD), Nitrogen physisorption, temperature programmed reduction (TPR) with diluted H_2 or CH_4 and temperature programmed oxidation (TPO) techniques. The Redox stability was checked with multiple REDOX cycles and chemical looping experiments were carried out isothermally alternating the gas composition every 10 minutes from 15 vol% of CH_4 in N_2 to air. The reaction temperature was chosen for each sample based on temperature programmed reduction measurements with methane.

Results and discussion. Characterizations of nickel based materials confirmed very different nickel enviroments whose redox stability, checked by two cycles of H_2-TPR/O_2-TPO, was very high for NiAlMg and $LaNi_{0.8}Co_{0.2}O_3$, and lower for the other trhee structures. Looking at the CH_4-TPR the best perfomances , in terms of hydrogen production, is given by NiCaAl and NiCe catalysts with a peak of activity at 600°C. The same behaviour was found in the reduction/oxidation cucles with CH_4/air mixtures, with the sample NiCaAl having the highest hydrogen yield. This sample suffered of a deactivation along the cycles, due to structural modifications, while NiCe showed a stable activity along ten redox cycles (see Fig. 1).

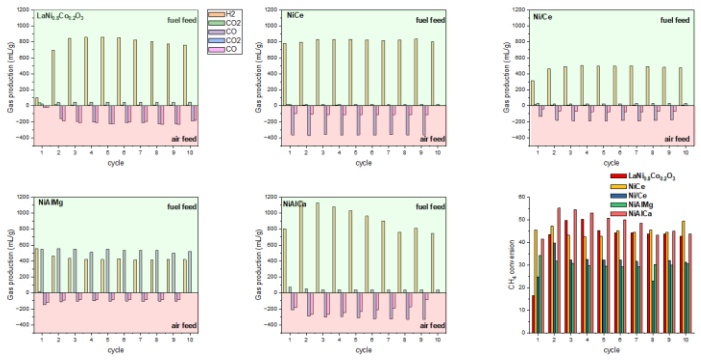

Fig. 1 Cycles fuel/oxidant over different catalysts

Acknowledgments

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Particle size effect for CO_2 hydrogenation by In_2O_3-ZrO_2 catalysts

Björn Baumgarten[1], Rune Lødeng[2], Edd A. Blekkan[1], Jia Yang[1]

[1]*Department of Chemical Engineering, NTNU, Sem Sælandsvei 4, 7491 Trondheim, Norway*
[2]*SINTEF Industry, Rickard Birkelandsvei 3, 7465 Trondheim, Norway*
**bjoern.baumgarten@ntnu.no*

Keywords: Carbon dioxide hydrogenation, Particle size effect, Indium oxide, Green Methanol

Introduction. To combat global warming, liberation of fossil CO_2 should be avoided. However, some processes require carbon as a raw material, which could instead be taken from the atmosphere or CO_2 emissions from industry.
One important reaction for this is the production of methanol from CO_2, either as a stand-alone process or coupled with e.g. MTO to produce methanol.
For CO_2 hydrogenation, Cu-based catalysts similar to those used for CO hydrogenation were used, but to overcome their drawbacks many new catalysts based e.g. on In_2O_3-ZrO_2, PdZn, ZrZn systems are being researched. Two main factors are identified that influence the selectivity and yield of the In_2O_3 system: As shown by Chen et al [1], CO formation mainly depends on the indium loading, or more precisely the particle size of the indium particles, as intermediates are suspected to spill over to the zirconia surface and decompose to CO and H_2O if the particles are too small. Additionally, the lattice spacing of m-ZrO_2 is almost half of the spacing of In_2O_3, which leads to high strain when an Indium layer is deposited on zirconia, improving the methanol activity [2]. Using a modified, green catalyst preparation method involving alginate as a template [3], highly dispersed In_2O_3 particles can be obtained at high loadings, demonstrating the importance of particle size instead of loading.
Experimental/methodology. Catalysts were prepared by mixing a Na-alginate gel with zirconia powder. Next, the alginate was ion-exchanged with indium, after which indium is finely dispersed in a matrix of alginate gel. During calcination, the alginate is burned off, thereby depositing indium particles on the zirconia powder. By varying the calcination duration and thus the degree of sintering, different particle sizes were prepared. In addition, impregnation catalysts were prepared by wetness impregnation as described by Martin et al [4]. For catalyst characterization, BET was used to measure the extent of sintering, while XRD and SEM were used to obtain particle size and changes in lattice parameters.
Results and discussion. Most of the current literature concentrates on the loading, even though already Chen et el. assumed the particle size is key. To understand the influence of the particle size, it is first required to synthesize catalysts with varying particle sizes without changing any other parameter. E.g., during the study of Chen et al., the particle size was changed indirectly by loading. However, preliminary results show that it is possible to deposit indium nanoparticles of a chosen size using the alginate method onto zirconia at a loading of 20 wt-% In_2O_3 (minimum size: 4 nm, after 8h sintering: 14 nm). As expected from the literature, the methanol selectivity was negatively correlated to the particle size. According to XRD results, the strain of the lattice is also negatively correlated.
An impregnation catalyst resulted in a particle size of 6 nm and an intermediate selectivity.
With additional data from alginate and impregnation catalysts with different particle sizes, more insight into the effects of the particle size for both the activity towards methanol and the selectivity will be obtained and presented.

Acknowledgments

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Electrified CO_2 reforming of methane and reverse-water gas shift driven by Joule heating

L. Zheng, M. Ambrosetti, F. Nicolini, A. Beretta, G. Groppi, E. Tronconi*
Dipartimento di Energia, Politecnico di Milano, Via Lambruschini 4, 20156, Milano, Italy
**enrico.tronconi@polimi.it*

Introduction. The CO_2 reforming of methane (dry reforming of methane, DRM) and the reverse water-gas shift (RWGS) reactions are interesting alternatives for syngas production from captured CO_2 [1]. To allow significant conversion, heat should be supplied to the reactor at relatively high temperature (700-800°C). Instead of using conventional fuel combustion which reduces the CO_2 valorization potential, we report here the catalytic CO_2 activation in a structured reactor driven by Joule heating, which paves a new path to the synthesis of low carbon chemicals utilizing captured CO_2 and excess renewable electricity.

Experimental/methodology. Like in our previous works on electrified methane steam reforming [2, 3], a SiSiC foam washcoated with Rh/Al_2O_3 catalyst was prepared and connected to an AC generator to provide efficient Joule heating combined with optimal heat and mass transfer properties for the catalytic CO_2 conversion (Fig. 1(a)). eDRM: CO_2/CH_4=4, eRWGS: H_2/CO_2=2.25, GHSV=100 kNl/kg_{cat}/h, ambient pressure.

Results and discussion. As shown in Fig. 1(b), the structured catalyst could be heated by the Joule effect up to temperatures needed for DRM and RWGS reactions. An almost linear correlation was observed between the input power and the measured outlet foam temperature, T_{cap}. As a result of its higher endothermic nature, the eDRM (ΔH=247 kJ/mol) require more power to reach the same temperature in comparison to eRWGS (ΔH=41 kJ/mol) at same GHSV. CO_2 conversions approaching equilibrium were measured across a wide range of conditions for both reactions (Fig. 1(c)). The eRWGS process was highly selective, as hardly any CH_4 could be detected for the investigated conditions. We ascribe these results to the high activity of Rh catalyts for both DRM and RWGS reactions, to the excellent external mass transfer properties combined with the intimate contact between catalyst and electrified foam support. The overall energy efficiency of the system was evaluated from the ratio of process heat duty (H_{out}-H_{in}) to input power (W_{el}). An energy efficiency of approx. 25% was obtained for eRWGS, while a higher value of approx. 53 % was achieved for eDRM. The heat dissipation is the primary source of energy loss in our system and, once the reactor geometry is fixed, it is mainly governed by the reactor temperature. We could demonstrate that losses are in a similar range for the two reactions, while the net process heat demand at the same GHSV is higher for eDRM, leading to a higher thermal efficiency. Noteworthy, such a dissipation mechanism can be minimized when scaling up the reactor. Moreover, the proposed electrified reactor concept is proven to ensure remarkably low specific energy demand for CO_2 valorization (approx. 0.7 kWh/Nm^3_{CO2} for eRWGS, considering an overall adiabacity of 95% and a recovery of 90% sensible heat).

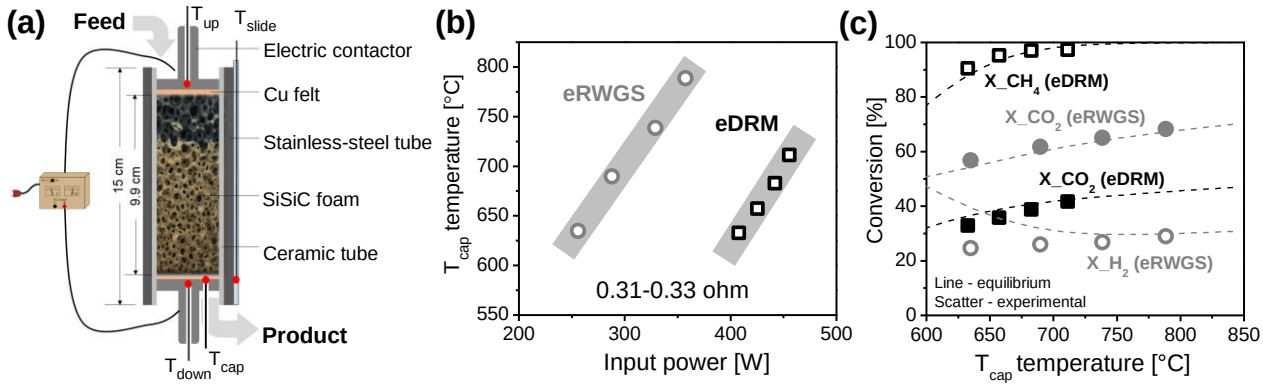

Fig. 1 (a) Electrified reactor layout, (b) T_{cap} vs. input power, (c) CO_2 conversion vs. T_{cap} during eDRM and eRWGS runs.

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Kinetic Modeling of CO_2 Hydrogenation via Fischer-Tropsch Synthesis Using K/Fe-Cu-Al Catalysts

Yubeen Jung[1], Yesol Woo[1], Hae-Gu Park[2], Ki-Won Jun[2], Jeong-Rang Kim[2], Myung-June Park[1,3]*

[1]*Department of Energy Systems Research, Ajou University, Suwon 16499, Republic of Korea*
[2]*C1 Gas & Carbon Convergent Research Center, Korea Research Institute of Chemical Technology, Daejeon 34114, Republic of Korea*
[3]*Department of Chemical Engineering, Ajou University, Suwon 16499, Republic of Korea*
**mjpark@ajou.ac.kr*

Keywords: CO_2 hydrogenation, Fischer-Tropsch synthesis, kinetic modeling, parameter estimation

Introduction. CO_2 hydrogenation via Fischer-Tropsch synthesis (FTS) is one of the ways to convert CO_2 to a high-value-added product, and hydrocarbon synthesis over Fe catalysts prepared by co-precipitation was shown to be promising in our previous work [1]. This work addresses the development of kinetic rate equations for CO_2 hydrogenation over K/Fe-Cu-Al catalyst to analyze the contribution of two different pathways and quantitatively evaluate the effects of operating conditions on the catalytic performance.

Experimental/methodology. Details about catalyst preparation and characterization can be referred to in our previous work [1]. Kinetic data were produced in the experiments (0.5 g of catalyst and 2 g of Al_2O_3) under various temperatures (270–330 °C), space velocities (1000–5000 mL/g_{cat}/h), and feed compositions ($H_2/CO_2/CO/Ar$ = 72/24/0/4 and 72/20/4/4), while pressure was fixed at 21 bar. The CO_2 conversion and the yields of methane, ethane, ethene, propane, propene, butane, butene, C_{5+}, and C_{5+}= were measured.

Results and discussion. The two different pathways were considered in this work; direct CO_2 hydrogenation to hydrocarbon products and reverse-water-gas-shift reaction followed by CO-FTS reaction. The Langmuir-Hinshelwood type rate equations were assumed for overall reactions, where CO, CO_2, H_2, and H_2O were considered in the site-balance equation. Kinetic parameters were estimated by fitting experimental data, in which lsqcurvefit function in Matlab (MathWorks Inc.) was used to apply the Levenberg-Marquardt method for the minimization of the objective function. The means of absolute relative residuals for the objective elements (conversion and yields) were less than 20%, and the model could satisfactorily describe the catalytic behaviors of CO_2 hydrogenation. Further analysis will be conducted to evaluate the effects of operating conditions and determine the optimal condition for high productivity of light olefins and stable thermal behavior in the reactor.

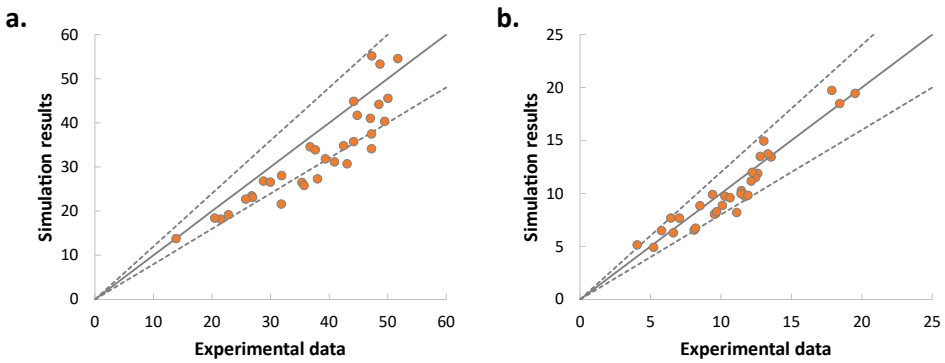

Figure 1. The comparison of **(a)** CO_2 conversion [%] and **(b)** C_{5+} yield [%] between experimental data and simulation results. The solid and dashed lines represent the diagonal and ±20% error lines, respectively.

Acknowledgments
This work was supported by the "Carbon Upcycling Project for Platform Chemicals" (Project Nos. 2022M3J3A1045999, 2022M3J3A1039377) through the National Research Foundation (NRF) funded by the Ministry of Science and ICT, Republic of Korea.

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Membrane reactor: A case study of methanol production

A. Pavlišič[1*], A. Prašnikar[1] and B. Likozar[1]

[1]*Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, 1001 Ljubljana, Slovenia*
[*]*andraz.pavlisic@ki.si*

Keywords: CFD, membrane reactor, reactor optimization

Introduction. Despite technological maturity, understanding reaction mechanism and the interplay of the surface properties is still ongoing topic among researchers. Thus, the exact mechanism of the reaction pathway and the interplay of the catalytic surface have received much attention in academia in recent years [2,3]. While multi-scale hierarchical approach was already successfully applied to a compelling industrial process, where catalytic heterogenous system is captured from micro to macro level, it is hard to believe that this will become a main stream of solving industrial processes due to high computational cost of the methods.

Experimental/methodology. On the other hand, correlation equations (CE) have a long history of use in chemical engineering. They are collection of dimensionless numbers and coefficients that gives fast and meaningful prediction of mass and heat transfer. The advantage of CE is that they project three dimensional phenomena to one dimension by averaging physiochemical properties which can be used in much simpler continuum fluid dynamic models such as plug flow reactor (PFR). However, they have to be experimentally determined for each specific system which in case of industrial scale reactors is prohibitively expensive. Moreover, CE validity is strictly bonded to the specific range of the operational conditions of the system.

Results and discussion. Herein we captured all the local phenomena which can be used to calculate CE with aid of CFD. The goal was to develop workflow for model order reduction (MOR) of computational demanding CFD model. Thus, mass and heat transfer obtained with CFD simulation was linked to pseudo-homogeneous and heterogeneous continuum models. With this technique we created modules for fast and targeted optimization of industrial processes.

Acknowledgments
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Bimetallic MOF-Derived Catalysts for Photo-thermal CO_2 Hydrogenation

F. Almazán[1], M. Lafuente[2], A. Echarte[1], M. Imizcoz[1], I. Pellejero[1*], L.M. Gandía[1]

[1]*Institute for Advanced Materials and Mathematics INAMAT[2], Universidad Pública de Navarra. Campus Arrosadia, 31006, Pamplona-Iruña, Spain*

[2] *Universidad de Zaragoza, Campus San Francisco, 50013, Zaragoza, Spain.*

[*]*Corresponding Author: ismael.pellejero@unavarra.es*

Keywords: Photo-thermalcatalys, Bimetallic MOFs, CO_2 hydrogenation

Introduction: The use of Metal-organic frameworks (MOF) as hard templates for the preparation of heterogeneous catalysts have attracted great attention in last years, due to the excellent features (high surface area or porosity) and the good and uniform distribution of metallic clusters in the derived structure [1,2]. Herein, we have prepared via calcination and pyrolisis several bimetallic MOF-based catalysts (Zr-BDC in combination with Ru and Ni) and we have tested for the photo-termal hydrogenation of CO_2.

Experimental/methodology: Bimetallic MOF were synthesized following published protocols for the monometallic UiO-66 MOF (Zr-BDC) [3] (BDC = terephthalic acid) with a metal to organic ligand ratio of 1 : 2 (metal : organic ligand). Guest specie Ru or Ni were introduced by interchanging 3 % or 10 % of the initial Zr precursor by the respecting salt ($RuCl_3$ or $NiCl_2$). Bimetallic MOFs were treated from 400 ºC to 600 ºC for 3 h in air atmosphere or in dry N_2. Physicochemical properties were characterized by XRD, TEM, TEM-EDX, TGA and ICP. Catalytic activity was evaluated by CO_2 photothermal hydrogenation (1 CO_2 : 4 H_2) in a Harrick chamber under 3 Suns of irradiance. The outlet gas was analyzed with an Agilent microGC.

Results and discussion: Figure 1 shows some examples of the CO_2 hydrogenation under some calcination treatments. The CO_2 conversion increased with increasing calcination temperature. The selectivity of Ru0.10ZrO2 treated at 600ºC was close to 100% at temperature of 300ºC. Under pyrolysis, MOF derived-carbons present high selectivity to CO formation.

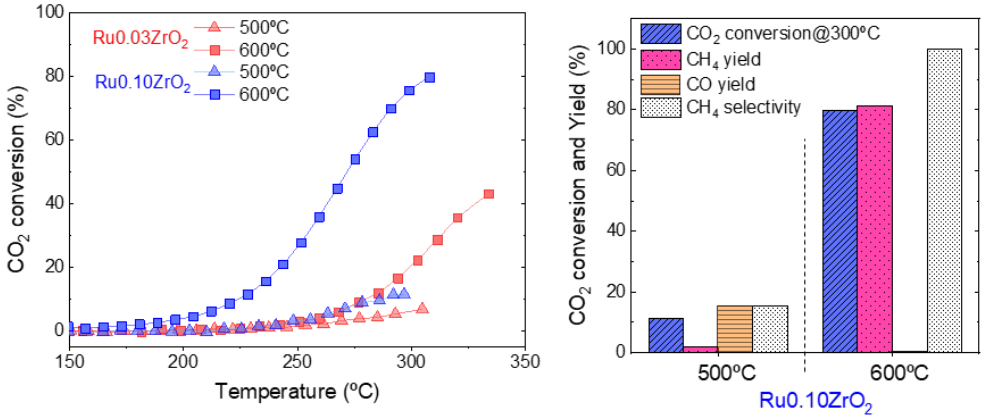

Figure 1. (a) CO_2 conversion of $Ru0.03ZrO_2$ and $Ru0.10ZrO_2$ catalysts calcinated at 500 °C and 600 °C at different reaction temperatures. (b) CO_2 hydrogenation activity of $Ru0.10ZrO_2$ catalysts calcinated at different temperatures under 300 °C reaction temperature.

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Promising electrocatalysts based on surface modified Zeolite Templated Carbons for CO_2 valorization

D. Chillè[1], P. Squillaci[1], G. Papanikolaou[1], E. Catizzone[2], M. Migliori[2], G. Giordano[2], G. Centi[1], S. Perathoner[1], P. Lanzafame[1]

[1]*Department ChiBioFarAm, University of Messina, V.le F. Stagno d'Alcontres 31, Messina 98166, Italy.*
[2]*Chem. Eng., Catal. and Sustainable Proc. Lab. – CECaSP_Lab, Univ. of Calabria, Rende (CS) 87036, Italy*
[*]*gpapanikolaou@unime.it*

Keywords: Electrocatalytic reduction of CO_2, Zeolite Templated Carbons, oxygen functionalities in ZTC

Introduction.

In the last years, the rapid increase of greenhouse gas emissions and sudden climate change is becoming one of the most critical issues to be addressed. The electrocatalytic conversion of CO_2 into high added value products such as formic acid (FA) represents a very promising technology to address this issues. From this perspective, the greatest challenge facing the scientific community is the development of new stable and low-cost materials to achieve this technology at industrial level. Zeolite templated carbons (ZTC) thanks to their high conductivity, high surface area and chemical stability can be considered promising candidates as electrocatalysts for the CO_2 valorization [1, 2].

Experimental/methodology.

Two different ZTCs were synthesized starting from a home made and a commercial Na-BEA zeolites (ZTC_01 and ZTC_02) through Chemical Vapour Deposition using ethylene as a carbon source at high temperature. A combination of a chemical and thermal treatment was carried out in order to modify the nature and the amount of the oxygen functionalities on the ZTCs surface. The effect of the surface modification was in depth investigated using different techniques as XRD, N_2 adsorption, TGA/DTA, SEM/EDS analysis, FT-IR and Raman spectroscopy. The electrocatalytic behavior of the electrocatalysts was evaluated in the electrocatalytic reduction of CO_2 in a three-electrode flow cell configuration (-1.6 and -1.8V vs Ag/AgCl) using 0.5 M $KHCO_3$ as catholyte and 0.5M H_2SO_4 as anolyte. The liquid and gas products were identified by HPCL and micro GC in line.

Results and discussion.

ZTCs were synthesised and further modified by a deoxygenation procedure using combined thermal and $NaBH_4$ treatment. Through a deep characterization was possible to observe how the combined treatments lead to a reduction of oxygen content obtaining a more ordered structures. From the electrocatalytic results was possible to assess how the induced surface modification of ZTCs coherently affects the electrocatalytic activity. The best electrocatalytic performances was obtained by using the treated sample (rZTC0_1) derived from the home made zeolite which reaches a 40% of faradaic efficiency to FA at -1.8V. Analising the obtained results it is highlited a direct correlation between the degree of order (I_D/I_G) of the structure calculated by Raman spectroscopy and the catalytic performances as well as a linear correlation with the amount of oxygen content. These results highlights how the surface modification of ZTCs represents a promising strategy for the development of efficient electrocatalysts for the CO_2 valorization.

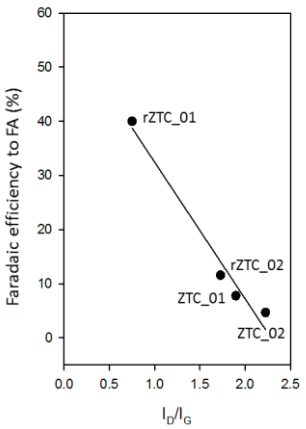

Fig.1: Correlation between the Faradaic efficiency and ZTCs order degree

Acknowledgments

G.P. would thanks the Ministry of University and Research (MUR) for the grant received in the frame of the project PON "Research and Innovation" 2014-2020 (Action IV.6 Research Contract on Green topics, D.M. n. 1062/2021).

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CO_2 driven light alkanes oxidative dehydrogenation over nickel and iron heterogeneous catalysts

M. Percivale[1], E. Spennati[1], P. Riani[2], R. Millini[1], G. Garbarino[*1]

[1] *Department of Civil, Chemical and Environmental Engineering, University of Genoa, Genoa, Italy*
[2] *Department of Chemistry and Industrial Chemistry, University of Genoa, Genoa, Italy*
[*] *gabriella.garbarino@unige.it*

Keywords: CO_2 hydrogenation, alkane dehydrogenation, heterogeneous catalyst

Introduction. In the recent years, an increasing attention has been paid to the sustainable development of cutting-edge technologies and processes with an increasingly reduced environmental impact, accounting also for the EU target of net zero emission by 2050 [1]. In principle, these technologies would make it possible to avoid emitting CO_2 into the atmosphere [2], through carbon capture and storage processes (CCS) or even by reusing it (CCU, Carbon Capture and Utilization) as a feedstock in the energy, chemical and building industries. In this complex scenario, different key-challenges need to be undertaken. Therefore, the aim of this work is to develop efficient catalysts in processes involving CO_2 as a reactant.

As a starting point of the study, a catalytic system that was already at the state of the art (heterogeneous Ni-, Fe-based and bimetallic catalysts [3,4]) was chosen, by focusing on different reactions, i.e. methanation, reverse Water Gas Shift (rWGS) and so-call tandem reaction (light alkanes oxidative dehydrogenation) in order to evaluate their performances. The great advantage of coupling light alkanes dehydrogenation to rWGS is that a process can be carried out without introducing hydrogen into the system, using CO_2 as a soft oxidant. This results in great benefits in terms of energy efficiency, process simplification, and costs.

Experimental/methodology. Ni-, Fe- and (Ni, Fe)-catalysts supported on CeO_2 have been prepared through Incipient Wetness Impregnation (IWI) technique using an aqueous solution of metal precursor salts and then calcined. In order to evaluate their morphology and structure, the catalysts have been characterized through XRD and FE-SEM analysis before and after the catalytic tests. Moreover, catalytic materials have been characterized by FT-IR and UV-vis techniques.

The catalysts have been tested in a laboratory-scale plant equipped with a fixed bed tubular reactor by evaluating the catalytic performances in CO_2 hydrogenation to methane and by attempting more challenging CO_2 conversion processes as well by the so-call tandem reactions, accounting for a complex mix of alkanes. Moreover, a thermodynamic equilibrium analysis of the catalytic system was carried out using AVEVA PRO II software® [5].

Results and discussion. All catalysts resulted to be active in the proposed reactions, despite the metal loadings. Therefore, it is possible to develop cutting-edge catalysts based on abundant, non-critical, and cheap transition metals by finely tuning composition.

Ni-based catalyst promotes rWGS reaction at low temperature ($T < 623$ K), while Fe-based at high temperature ($T > 623$ K). Ni addition into Fe-based catalysts increases catalytic stability and activity to rWGS, reaching CO yields close to the equilibrium one.

Considering the tandem reaction system, higher catalytic activity to rWGS and dehydrogenation reactions has been obtained using the bimetallic catalyst compared to the Ni-based one, even though the first undergoes faster deactivation.The phenomena underlying this behavior are not known to date and work is in progress to clarify this important issue.

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Synergetic Activity of Ag and Zn in CO_2 Hydrogenation to Methanol

S. Phadke[1,2], C. Copéret[2], O. V. Safonova[1]

[1] *Paul Scherrer Institut, CH-5232 Villigen, Switzerland*
[2] *ETH Zürich, Laboratory of Inorganic Chemistry, CH-8093 Zürich, Switzerland*

Keywords: silver, zinc, CO_2 hydrogenation, methanol

Introduction: The search for a highly-efficient CO_2-to-methanol hydrogenation catalyst has led scientists to screen different bimetallic compositions, mainly consisting of Cu, Pd, Ni and Au nanoparticles promoted with various promoters such as Zn, Ga, Zr, etc. However, Ag, the element sandwiched between Cu and Au, has been much less considered among the coinage metals. In this work, we attempt to uncover the activity of Ag in combination with Zn for the selective hydrogenation of CO_2 to methanol.

Experimental/Methodology: In contrast to Cu-Zn bimetallic system, very little is known about the synergy of zinc and silver. We synthesized a series of Ag-Zn catalysts supported on silica with constant Ag and varied Zn loading. The catalysts were tested in a flow reactor at 40 bar CO_2:H_2:Ar = 1:3:1 at 250°C. Quasi *in situ* XAS analysis was performed at Zn and Ag K-edges for the calcined and H_2 activated (at 350°C) catalysts. (S)TEM and EDX mapping were implemented to visualize the distribution of Ag and Zn.

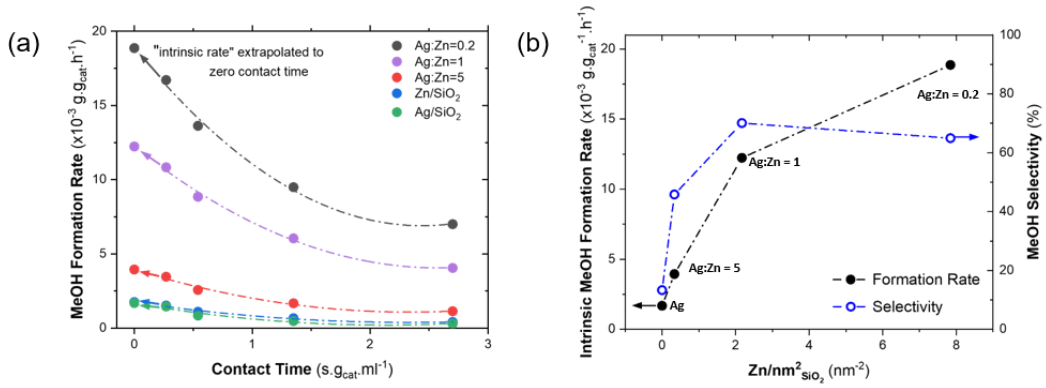

Figure 1: Methanol (MeOH) formation rate for the series of Ag-Zn/SiO_2 catalysts as a function of contact time (arrows indicate intrinsic methanol formation rate at zero contact time obtained by a second-order polynomial fit of formation rates); (b) Intrinsic MeOH formation rate and MeOH selectivity as a function of nominal Zn surface coverage. The samples are denoted by Ag:Zn molar ratios; Ag concentration is ca. 7wt%.

Results and Discussion: Neither Ag nor Zn are very active in CO_2 hydrogenation and selective for the formation of methanol. Adding Zn to Ag/SiO_2 steadily increases the methanol formation rates. The methanol selectivity, the other product being CO, seems to plateau after 2 Zn/nm^2 support coverage. According to XAS and TEM, Ag is easily reducible and forms Ag nanoparticles of ca. 2.8 nm without evidence of alloying with Zn. From XAS, it is also apparent that Zn exists only in a cationic Zn^{II} state, even after H_2 activation at 350°C. This cationic Zn^{II} is composed of a mixture of isolated Zn^{II} sites on silica and highly dispersed ZnO oligomers with an incomplete second Zn-O-Zn coordination shell. The latter is visible in HAADF-STEM images of the catalyst with the highest Zn loading (Ag:Zn = 0.2), and its location coincides with the Ag nanoparticles. For the lower Zn loading (Ag:Zn = 1), crystalline domains of ZnO are not detectable. We hypothesize that the ZnO phase presenting at higher Zn loading and its characteristic interface with the Ag nanoparticles are crucial for catalyzing the hydrogenation of CO_2 and the formation of methanol. We are currently probing the structure of the Ag-Zn system using *in situ* XAS and IR spectroscopy to further elucidate the specific function of each phase, clarify the reaction mechanism of methanol formation, and compare the reactivity of Ag-Zn and Cu-Zn systems.

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A synergistic interplay between Ag and Re supported on TiO_2 promotes methanol selectivity in low temperature CO_2 hydrogenation

N. Phongprueksathat[1], L.C. Wirner[1], S.M. Phadke[2], O.V. Safonova[2], A. Urakawa[1*]

[1] *Catalysis Engineering, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, Netherlands*
[2]*Paul Scherrer Institute, Villigen PSI, 5232, Switzerland*
[*]*A.Urakawa@tudelft.nl*

Introduction

Currently, conventional $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis from syngas are employed for commercial-scale CO_2 hydrogenation to methanol, under conditions of 200-300 °C and 10-100 bar [1]. According to Le Châtelier's principle, lower temperatures are more favorable to achieving almost full CO_2 conversion and CH_3OH selectivity [2]. However, the major challenge is overcoming the sluggish kinetics, thus leading to the exploration of highly active and selective catalysts below 200 °C. Re/TiO_2 was the most promising in reactivity under a batch condition (44 TON, S_{CH3OH} = 82%, H_2/CO_2 =5, 150 °C, and 60 bar) among various supported metals (e.g. Pt, Pd, Rh, Ir, Ru, Ni, Co, Ag, and Cu), supports (e.g. ZrO_2, SiO_2, Al_2O_3, CeO_2, etc.), and the conventional $Cu/ZnO/Al_2O_3$ catalyst, because the subnanometer size Re with multi-oxidation states between Re^0 and Re^{4+} served as active sites for methanol formation [3].

Experimental

The catalyst synthesis of Cu, Rh, Pd, Ag, Re, Pt, and Au supported on TiO_2 was prepared via the wet impregnation method, as reported elsewhere [3]. The catalysts were reduced *in situ* under H_2 at 500 °C, tested in a fixed-bed reactor at H_2/CO_2 = 3, 125-200 °C, 60 bar, and characterized by XRD, H_2-TPR, TEM, STEM-EDS, *Ex situ* XAS, and *operando* DRIFTS.

Results and discussion

Among various M/TiO_2 (M = Cu, Rh, Pd, Ag, Re, Pt, or Au), Re/TiO_2 remained the most active and selective catalyst for CH_3OH. The origin of the unique reactivity of Re/TiO_2 was elucidated previously as the coexistence of cationic highly-dispersed Re including single atoms, driving the formation of monodentate formate, and metallic Re clusters in the vicinity, activating the hydrogenation of the formate to methanol. The ability to stabilize formate species against its decomposition to CO was reflected in a high methyl formate selectivity at low temperatures over Re/TiO_2 and $Cu/ZnO/Al_2O_3$; (125 °C), which was found over Ag/TiO_2 at increasing temperatures (175 °C). The addition of a small amount of Ag to Re/TiO_2 improved the methanol selectivity significantly by suppressing methane formation. STEM-EDS showed that Re clusters migrated and distributed around the Ag nanoparticles over $Re\text{-}Ag/TiO_2$ after the reaction. *Ex situ* XAS reveals no alloy formation between Re-Ag after reduction. After CO_2 hydrogenation, Ag remained metallic while Re was oxidized creating cationic Re species. *Operando* DRIFTS studies confirm that the reaction mechanism over $Re\text{-}Ag/TiO_2$ is identical to that of Re/TiO_2 but metallic Ag addition helps boost forming surface formate species while suppressing carbonyl species which is the intermediate for methane formation. Metallic Re species act as H_2 activators, leading to H-spillover and importantly to hydrogenation of active formate intermediate present over cationic Re species. The role of metallic Ag is ascribed to complementarily activate CO_2 to formate and supply it to cationic Re species via spillover, driving forward the hydrogenation of the formate to methanol. $Re\text{-}Ag/TiO_2$ showed high stability in CO_2-to-methanol and improved catalytic performance over time on stream up to 40 h. This work has important implications for other bifunctional systems where the balance between different catalytic functions determines the rates and product distribution.

Acknowledgments

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Exceptionally High Productivity of ZrO_2 Supported Au Catalysts in CO_2 Hydrogenation to Methanol

T. V. Sagar[1], J. Zavašnik[2], M. Finšgar[3], N. Novak Tušar[1], A. Pintar[1*]

[1]*National Institute of Chemistry, Ljubljana, Slovenia*
[2]*Jožef Stefan Institute, Ljubljana, Slovenia*
[3]*Faculty of Chemistry and Chemical Engineering, University of Maribor, Maribor, Slovenia*
[*]*albin.pintar@ki.si*

Keywords: CO_2 hydrogenation, methanol synthesis, Au/ZrO_2, *in-situ* DRIFTS, CO_2 utilization

Introduction. Carbon pollutants production via the utilization of carbon-based fuels has enormously increased since the industrial revolution. These carbon effluents released into the atmosphere are among the main factors responsible for global warming through the greenhouse effect. The global temperature rise due to global warming drives the scientific community to find strategies to reduce CO_2 emissions and the level of CO_2 in the atmosphere. In this regard, CO_2 is considered as an abundant C1 source that can be used as a raw material to produce vital value-added products, such as syngas, dimethyl ether, formic acid, methane, higher hydrocarbons, methanol, etc. The use of CO_2 as a feedstock can be seen as advantageous from both environmental and economic points of view to achieve carbon neutrality, contributing to global climate change mitigation. CO_2 conversion has several advantages and challenges; therefore, it is necessary to discover new concepts and opportunities for catalytic and industrial development. Among all the CO_2 conversion routes, most studies in recent years have been focused on CO_2 hydrogenation to methanol [1].

Experimental/methodology. Amorphous ZrO_2 supported 0.5-1 wt.% Au catalysts were synthesized in the present work by two preparation methods, namely deposition precipitation (DP) and impregnation (IMP), characterized by a variety of techniques and examined in the process of CO_2 hydrogenation to methanol.

Results and discussion. The use of nanometric gold nanoparticles supported on ZrO_2 enables efficient hydrogenation of CO_2 to methanol even at low temperatures. Au deposition decreased specific surface area due to pore blockage; this decrease was considerably low in the case of DP method. TEM analysis revealed that Au particle size distribution depends on the preparation method and Au loading, with the DP technique resulting in the formation of Au ensembles with 1 nm in size. TPD measurements illustrated a change in the strength and number of surface acidic and basic sites with the deposition of Au; these changes were strongly influenced by the method of preparation, where the catalysts synthesized by the DP technique showed strong acidic sites and a high number of basic sites (i.e. Zr^{4+}/O^{2-} centres). Variations in surface sites due to different preparation methods exhibited a huge impact on the formation of intermediates and their fast hydrogenation to methanol. Important surface intermediates were identified by *in-situ* DRIFTS analysis, i.e. formate, dioxymethylene and methoxy species, which helped to establish a possible reaction mechanism via the formate route [2]. Here, time resolved FTIR profiles of both 0.5 wt.% Au loaded catalysts showed large differences in the hydrogenation of formate and methoxy intermediates with respect to the catalyst preparation method. High CO_2 uptake and the presence of small Au nanoparticles enabled fast hydrogenation of intermediate species to methanol over DP-based catalysts, whereas low CO_2 uptake and the presence of bulk Au clusters on the catalyst surface leads to slow hydrogenation of intermediate species to products, as observed in the case of IMP-based catalyst. Au/ZrO_2 catalysts synthesized by the DP method were advantageous in the process of CO_2 hydrogenation to methanol, compared to the IMP-based catalyst. Finally, the rate of formation of methanol was enhanced with increased synergy between the metal and support, and exceptionally high space-time yields of methanol (up to 2.0 $g_{MeOH}\ h^{-1}\ g_{cat}^{-1}$) were obtained in the presence of DP-based Au/ZrO_2 catalysts.

Acknowledgments
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CO_2 methanation catalysts derived from Ni-alkaline earth metal carbonates

Sharad Gupta[1*], Manon Gregoire[1], Sebastien Royer[2], Edmond Abi-Aad[1], and Christophe Poupin[1]

[1]*Université du Littoral Côte d'Opale, Unité de Chimie Environnementale et Interactions sur le Vivant (UCEIV), UR4492, 145, Avenue Maurice Schumann, Dunkerque 59140, France*

[2]*Université de Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181-UCCS-Unité de Catalyse et de Chimie du Solide, Lille 59000, France*

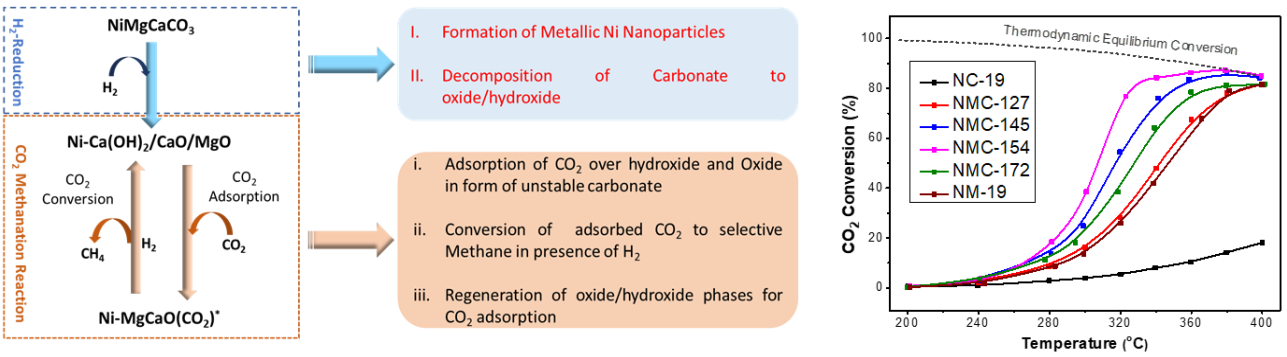
[*]*sharad.gupta@univ-littoral.fr*

Keywords: CO_2 methanation, Ni-based catalyst, Alkaline-earth metal carbonates

Introduction. The continuous increase in the world energy demand has increased greenhouse gases mainly CO_2 into the atmosphere. There is a pressing demand across the globe to develop materials and processes to reduce the harmful emission[1]. CO_2 methanation using a catalyst obtained from earth-abundant materials offers a promising option to economically reduce anthropogenic CO_2. Alkaline earth metal carbonates are interesting and relevant candidates with respect to CO_2 methantion as it is available in large quantities in the form of low-cost natural mineral resourses[2]. In this work, we have explored the use of supported Ni catalysts derived from alkaline earth metal carbonate. We obtained the catalysts from the thermal decomposition of respective carbonate precursors under H_2 stream and studied its catalytic activity and stability in CO_2 methantion reaction.

Experimental/methodology. $NiMgCaCO_3$ with different Ni:Mg:Ca ratios (NMC) were synthesized via a simple co -precipitation method using Na_2CO_3 as the carbonating agent. Under H_2 reduction condition, $NiCaMgCO_3$ decomposed to $Ni/Ca(OH)_2$-CaO/MgO and formed an active catalyst for CO_2 methanation. Under reaction condition hydroxide/oxide phase adsorbs CO_2 and formed a carbonate phase, which cyclically converted into oxide with the release of CH_4 in the presence of H_2 and metallic Ni.

Results and discussions. Screening of catalysts revealed that the active Ni catalyst originating from the decomposition of $MgCaCO_3$ exhibited good activity for CO_2 methanation. At 340 °C, NMC-154 showed 84% CO_2 conversion and 99.7% CH_4 selectivity. The developed catalytic system operated efficiently over 100 h on a stream without catalyst deactivation. Detailed structural characterization of these catalysts showed the phase-dependent generation of active species. From XRD and BET analysis it is revealed that, an increasing concentration of Mg in carbonates improves the textural properties and dispersion of Ni nanoparticles. The local reducing environment generated by the formation of CH_4 from the decomposition of alkaline metal carbonates maintains the reducibility of the catalyst. However, more detailed characterization studies must understand the structure-activity correlation of catalysts.



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Optimizing Cu_xO-doped TiO_2 materials for CO_2 photoreduction in a thin film flow reactor

J. Chávez-Caiza[1], J. Fernández-Catalá[1], M. Navlani-García[1], Á. Berenguer-Murcia[1*], D. Cazorla-Amorós[1]

[1]*Materials Science Institute and Inorganic Chemistry Department, University of Alicante, Ap. 99, E-03080 Alicante, Spain*

[*]*Corresponding author. E-mail: a.berenguer@ua.es*

Keywords: Photocatalysis, CO_2, CH_4, flow reactor, heterojunction

Introduction.

One of the key strategies identified in the scientific literature to alleviate climate change is the exploration of new catalytic reactions in which wastes may be converted into useful products [1-2]. In this respect, the reduction of CO_2 into useful chemicals appears as an ideal solution, and given the high amount of energy provided by the Sun, photocatalysis stands out as an ideal candidate to its application in energy-related research.

While titanium dioxide (TiO_2) is one of the most widely studied catalysts due to its numerous advantages, it is not without drawbacks, being perhaps the most grievous the fact that its light absorption capacity in the visible range is very limited due to its relatively large band gap (3.2 eV). For this reason, substantial efforts have been dedicated to the development of novel photocatalysts with enhanced visible light adsorption by the use of different dopants such as noble metals or transition metal oxides [3].

The objective of the present work is to prepare a series of photocatalysts based on the combination of TiO_2 and Cu_xO, in order to develop high-performance heterojunction systems. The photocatalysts were tested in the photoreduction of CO_2 in a flow reactor that uses a thin layer of the photocatalyst, thus being considered as a 2-dimensional flow reactor designed to irradiate the sample with UV LED lights during the experiments.

Experimental/methodology.

The impregnation of a transition metal (Cu) on the surface of TiO_2 (P25 Degussa) was carried out by a modification of a standard impregnation protocol followed by a reduction step with $NaBH_4$ [4]. The performance of the prepared photocatalysts in the reduction of CO_2 in the presence of water vapor to yield CH_4 using a flow reactor was evaluated under ambient conditions [3].

Results and discussion.

The first results obtained in our study were already promising considering those reported in the literature for such a process using similar reactor configurations (over 1 $\mu molCH_4 \cdot g\ cat^{-1} \cdot h^{-1}$), but the selection of a proper hole scavenger and the subsequent optimization of its concentration has allowed us to reach CH_4 production rates which are among the best reported irrespective of the reactor and/or conditions (117 $\mu molCH_4 \cdot g\ cat^{-1} \cdot h^{-1}$) and using low power LED lighting, which shows the outstanding relevance of our results. The effect of Cu loading and particle size has also been studied.

Acknowledgments

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Effect of substrate conductivity on charge transfer and CO_2 photoreduction to methane in water vapor over silica-modified TiO_2 films

Piyasan Praserthdam[1]*, Mohammad Fereidooni[1], Oswaldo Núñez[1], Victor Márquez[1], C.V. Paz[1], Martin Salazar Villanueva[2], Myo Zin Tun[3], Pongsakorn Kanjanaboos[3], Supareak Praserthdam[1,4]

[1]*Center of Excellence on Catalysis and Catalytic Reaction Engineering. Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. Bangkok 10330. Thailand.*
[2]*Facultad de Ingeniería, Benemerita Universidad Autonoma de Puebla, Apartado Postal J-39, CP 72570 Puebla, Mexico.*
[3]*School of Materials Science and Innovation, Faculty of Science, Mahidol University, Nakhon Pathom, 73170, Thailand.*
[4]*High-Performance Computing Unit (CECC-HCU), Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. Bangkok 10330. Thailand.*
[*]*Corresponding Author's E-mail address: piyasan.p@chula.ac.th*

Keywords: CO_2 reduction, methane production, Photocatalyst, Substrate's conductivity, Charge transfer, SPR.

Introduction. Recycling accumulated CO_2 in the atmosphere into value-added chemicals via a photocatalytic process is an ambitious strategy for mitigating both global warming and the energy crisis[1]. while supported photocatalysts on various soft or hard substrates for enhanced practicality have been successfully developed, the activity of the catalyst is attributed to the catalytic layer and the substrate's contribution to the catalyst's activity is less studied. When the thickness of the catalytic film is within the thin film domains, the substrate's role becomes more pronounced. Conductive substrates can function as electron collectors [2] in a multistep, complex reaction like the CO_2 photocatalytic reduction to decrease the recombination of charge carriers and to supply electrons to energy levels above or below the conduction band of the overlay catalyst (each intermediate of CO_2 reduction reaction has a different reaction potentials). Moreover, surface plasmon resonance (SPR) in certain conductive substrates [3] may improve the light-harvesting capability and catalyst's activity when thin film structure is used.

Experimental/methodology. Silica-modified amorphous and crystallized TiO_2 photocatalysts were spin coated on Ti sheet, indium tin oxide coated polyethylene terephthalate (ITO-PET), and PET substrates. The prepared films were employed in photocatalytic CO_2 reduction in vapor-phase and batch reactor. Optical and photo-electrochemical analyses, as well as simulations based on density functional theory (DFT), were used to investigate the effect of substrate conductivity on catalyst activity.

Results and discussion. On Ti sheet, photocatalysts' activity for CO_2 reduction to CH_4 and CO were significantly higher than on two other substrates. The photoluminescence (PL) analysis demonstrated that the substrate can significantly affect both the energy levels from which radiative recombination occurs and the recombination of charge carriers. The excitation of electrons to higher energy states can provide greater driving force in CO_2 reduction reaction and increase the catalyst's activity. Additionally, a study of the open circuit potential decay (OCPD) of the silica-modified crystalline TiO_2 revealed the function of the Ti substrate in electron collection. Moreover, the density of states (DOSs) modeling of the Ti substrate revealed the presence of intense energy states in the middle of the band gap of photocatalysts, which can facilitate electron transfer between the catalysts and substrate. By emphasizing on the substrate's effect in thin film photocatalysts, this study proposes a straightforward and effective approach for enhancing the photocatalytic activity for CO_2 reduction in water vapor.

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Atomic layer deposited zinc over metal oxide supported copper for carbon dioxide hydrogenation to methanol: Comparison of supports

Ahmed Sajid[1], Aitor Arandia[1], Jihong Yim[1], Ashish Chahal[1], Hua Jiang[1], Reetta Karinen[1], Riikka L. Puurunen[1*]

[1]*Aalto University, 02150 Espoo, Finland*
[*]*Riikka.puurunen@aalto.fi*

Keywords: Atomic layer deposition, metal oxide supports, zinc copper catalysts.

Introduction. Zinc-copper-based heterogeneous catalysts are well-known for carbon dioxide hydrogenation to methanol (CHM). Metal oxide supports can influence the activity of zinc-copper catalysts e.g. by affecting the reducibility of Cu and the CO_2 adsorption capacity [1]. In a recent work, adding zinc by atomic layer deposition (ALD) [2] on top of zirconia-supported copper to make "inverse" ZnCu catalysts was found beneficial for activity and selectivity in CHM [3]. In this work, continuing from the earlier work, we investigated the effect of support on heterogeneous inverse ZnCu catalysts for CHM.

Experimental. Copper was impregnated on metal oxide supports (alumina, ceria-zirconia, lanthana-ceria-zirconia, niobia, titania, zirconia) by incipient wetness impregnation and zinc was added by ALD. Catalysts were designed to have a Cu/Zn atomic ratio of 2, with ~2 Zn/nm^2 added by ALD [3]. This gave catalysts with 1.5-5.7 wt-% of Cu, depending on the support's surface area. Samples were characterized by N_2 physisorption, inductively coupled plasma-optical emission spectroscopy, hydrogen temperature programmed reduction, carbon dioxide temperature programmed desorptionand scanning transmission electron microscopy. Conversion, selectivity and methanol space time yield (STY) were measured in a continuous flow fixed bed reactor.

Results and discussion. The catalytic activity was influenced by the support. In terms of methanol STY, the metal oxide suppports gave highest activity in the order: zirconia > 17%ceria-zirconia > 25%ceria-zirconia > lanthana-ceria-zirconia > alumina > niobia > titania (Figure 1a). Addition of zinc on copper increased the activity in varying degrees: for example, on zirconia, the effect was minor whereas on niobia it was significant (Figure 1b). The highest methanol STY calculated per grams of copper was obtained on zirconica-supported ZnCu catalysts (124 mmol g_{Cu}^{-1} h^{-1}, at 550 K).

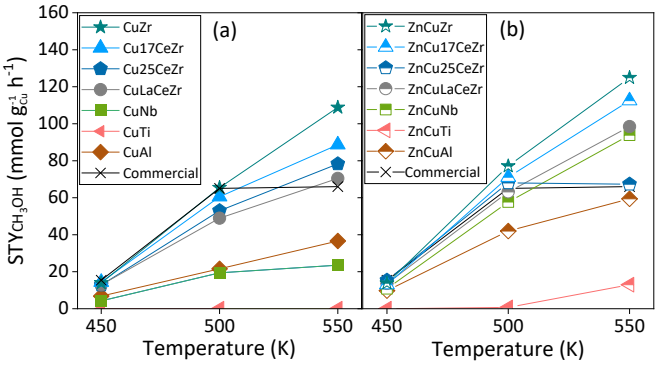

Figure 11: Methanol STY over supported (a) Cu and (b) ZnCu catalysts. Reaction conditions: *T* = 450, 500, 550 K, *P* = 3.0 MPa, $H_2/CO_2/N_2$ = 71/23/6 V/V/V%, space velocity = 8900 l g_{cat}^{-1} h^{-1} and m_{cat} = 1.0 g. The reaction was carried out for 90 minutes at each temperature.

Acknowledgments
This work was financed by the Academy of Finland (COOLCAT and ALDI projects).

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CO_2 activation *via* oxidative dehydrogenation and dry reforming of ethane over Fe_3Ni_1 nanoalloys influenced by supports

Shaine Raseale[1], Gonzalo Prieto[2], Michael Claeys[1] and Nico Fischer[1]*

[1]*Catalysis Institute and DSI-NRF Centre of Excellence in Catalysis c*change, University of Cape Town, Cape Town, South Africa.*
[2]*Instituto de Technología Química (ITQ), Av. de los Naranjos, 46022, Valencia, Spain.*
[*]*nico.fischer@uct.ac.za*

Introduction. The CO_2-mediated oxidative dehydrogenation of ethane (CO_2-ODHE) is an alternative route for producing the high-demand ethylene while simultaneously serving as a carbon capture and utilization (CCU) route co-activating CO_2 to CO. It has been extensively investigated on metal-oxides (MOx) with those based on Cr, V and Ga exhibiting promising selectivity towards ethylene but deactivate rapidly due to their low CO_2 activation ability [1]. The reaction proceeds *via* a Mars van Krevelen mechanism where the MO_x is reduced upon ethane activation and subsequently re-oxidized *via* CO_2 activation. Thus, desirable catalysts should possess suitable redox properties [2]. Since redox properties are interlinked with the Lewis acidity and in turn depend on the nature of MO_x, variation of Lewis acidity should influence activity (re-oxidation rate) under CO_2-ODHE. Recent studies identified supported Fe_xNi_y alloys as potential catalysts which depending on x:y ratio and support can promote either CO_2-ODHE or ethane dry-reforming (DR) with enhanced CO_2 activation [3-4]. However, not enough supports were explored to explicitly underpin their catalytic role. In this study, monodisperse Fe_3Ni_1 nanoalloys anchored on MO_x overlayers with varying Lewis acid strength were synthesized and tested for CO_2-ODHE.

Experimental/methodology. The nanoalloys were supported on MO_x overlayers which were coated on γ-Al_2O_3 using incipient wetness impregnation to impose uniform textural properties (surface area, pore volume and diameter) across different catalysts thereby decoupling their catalytic influences. To encourage effective alloying upon reduction, oxidic Ni-ferrite nanoparticles, in which Fe and Ni are closely associated, were prepared and used as alloy precursors. A benzyl alcohol solvothermal synthesis was employed to prepare the precursor nanoparticles before deposition onto the supports [4].

Results and discussion. Our results reveal that the initial activity of the bare overlayers increases with the Lewis acid strength and reducibility but is lost fast due to their low CO_2 conversion. The deposition of the Fe_3Ni_1 nanoalloys to the overlayers enhances the activity and stability due a significantly enhanced CO_2 conversion ability while the acidity vs activity trend is maintained. However, due to the significantly enhanced CO_2 conversion, the CO-forming DR reaction is prominent on the strongly acidic and reducible VO_x and CrO_x while CO_2-ODHE is predominant on the irreducible, GaO_x, TiO_x and SmO_x with intermediate to weaker Lewis acid sites. Thus, acidity and reducibility of MO_x supports play a key role.

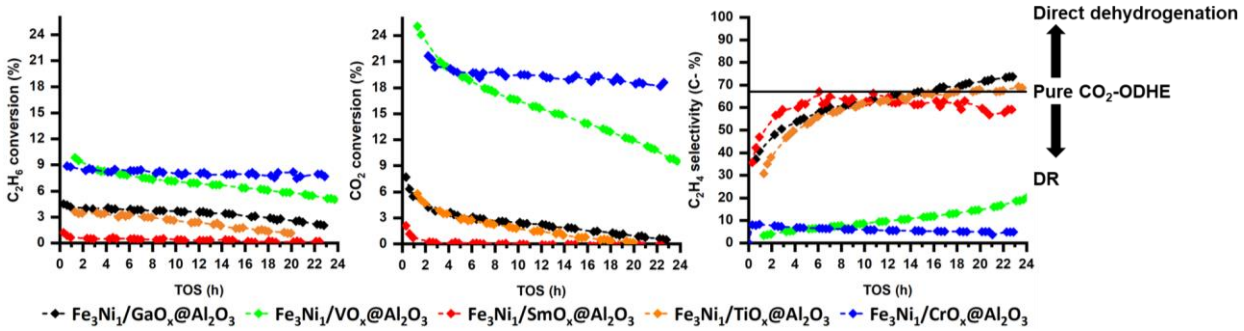

Figure 11: C_2H_6 (left) and CO_2 (middle) conversions and carbon based C_2H_4 selectivity of materials tested. Conditions: T = 600 °C, P = 1 atm, total space velocity = 15 $L \cdot h^{-1} \cdot g_{cat}^{-1}$, CO_2 : C_2H_6 ratio = 1 (6.25 mL/min each) with inert dilution.

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Carbon dioxide reduction *via* the reverse Water Gas Shift reaction over iron-nickel nanoalloy-based catalysts

Shaine Raseale, Karina De Kock, Michael Claeys and Nico Fischer*

*Catalysis Institute and DSI-NRF Centre of Excellence in Catalysis c*change, University of Cape Town, Cape Town, South Africa*
**nico.fischer@uct.ac.za*

Introduction. CO_2 emissions, primarily due to anthropogenic activities, have led to its increased atmospheric concentration (< 415 ppm currently) [1]. Currently, it is majorly accepted as a greenhouse gas linked to global warming, climate change and ocean acidification. Thus, multiple treaties such as the Paris agreement aiming to significantly reduce the global net CO_2 emission in the next decades to curb the global temperature increase to below 2 °C have been established. Some of the ways to realize this are CO_2 capture and storage (CCS), use of gas over coal and adoption of renewable energy sources. Another alternative with potential economic benefits is carbon capture and utilization which leverages on CO_2 as a carbon source for value-added chemical production. Several CCU processes such the Solvay method, methanol and urea synthesis, salicylic acid and cyclic carbonates production are already in industrial application but utilize a negligible fraction of the CO_2 emitted [2, 3]. Thus, the development of more CCU processes remain a necessity. Power-to-Liquid (PtL), which targets the production of liquid fuels using captured CO_2 with green H_2 *via* routes like the reverse Water-Gas Shift (rWGS) linked with the Fischer-Tropsch synthesis (FTS) reactions, can serve this purpose. However, the rWGS reaction is thermodynamically limited. Supported Fe_xNi_y alloys have shown potential for application as rWGS catalysts with the performance being metal composition dependent [4]. To extent the scope and understanding of their catalytic roles for future catalysts design, this study investigates the influence of metallic composition and support on the performance of Fe_xNi_y nanoalloys in the rWGS reaction.

Experimental/methodology. The nanoalloys are supported on a series of metal oxide (MO_x) ovelayers prepared by incipient wetness impregnation and are compared to commercial bulk oxides. To encourage effective alloying upon reduction, oxidic Ni-ferrite nanoparticles in which Fe and Ni are closely associated, were prepared and used as alloy precursors. A solvothermal synthesis in benzyl alcohol was employed to prepare the precursor nanopaticles before deposition onto the supports and reduced in situ before testing.

Results and discussion. Our results reveal a composition and support dependent tandem effect between the Fe_xNi_y alloy and reducible supports, significantly influencing the rWGS activity and stability of the catalysts. On the unreducible and inert SiO_2, the alloys deactivate fast with an overall low activity. However, the rWGS activity and stability increase slightly with increasing Fe-content. On GaO_x which has a high intrinsic activity and stability, the same trend with iron content is observed with a high stability maintained. However, the trend is reversed on the reducible CrO_x. The bare support shows some initial activity but is significantly more stable in the presence of the alloy, especially at an Fe:Ni ratio of 3. When studied on a larger library of supports, Fe_3Ni_1 shows a high rWGS activity and stability on the reducible overlayers (due to the tandem effect). However, poor stability/activity are observed on the unreducible supports. For all materials, a close to 100 C-% CO selectivity was obtained confirming the kinetic suppression of the methanation reaction.

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Selective production of isobutene – Isosynthesis over zirconia

N. Heikkinen[1], L. Keskiväli[1], R. Ikonen[2], B. A. Baraiya[2], V. Korpelin[2], T. Kiljunen[2], K. Honkala[2], M. Reinikainen[1*]

[1]*VTT Technical Research Centre of Finland, P.O. Box 1000, 02044 VTT, Espoo, Finland*

[2]*Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, 40014, Jyväskylä, Finland*

[*]*matti.reinikainen@vtt.fi*

Introduction. There is an ever-increasing need for sustainable fuels and chemicals. Many of the technologies such as the Fischer–Tropsch synthesis suffer from poor selectivity and, consequently, bad profitability. Isosynthesis, the highly selective process for the manufacture of isobutene and -butane, was discovered already in the 1940s [1], but it has not received very much attention. Over the decades, the extreme reaction conditions and harmful catalysts, about 300 bar and ThO_2-catalysts, have been replaced by more feasible and practical alternatives, while having better catalytic performance [2]. Due to these developments and recent demand for renewable feedstock conversion routes, isosynthesis has again become an interesting topic. This paper reports experimental work using syngas produced from CO_2 via reverse-WGS as well as computational results of isosynthesis reaction over a range of zirconia-based catalysts.

Experimental/methodology. Monoclinic and tetragonal ZrO_2, as well as Ce-, La- and Y-doped ZrO_2 were tested for isosynthesis reaction in a tubular fixed bed reactor. Reaction conditions varied between 400–450 °C, 20–45 bar and GHSV 2000–3000 h^{-1}. CO conversion and product selectivities were analyzed by on-line GC. In order to better understand the reaction mechanism and parameters affecting catalyst activity, the isosynthesis reaction network was also explored computationally using vdW-corrected DFT. Monoclinic ZrO_2(−212) was chosen as the model surface to account for the possible role of edge sites.

Results and discussion. Monoclinic ZrO_2 (450 °C, 45 bar, GHSV = 2000 h^{-1}) performed best out of the tested catalysts and iso-C4-hydrocarbons could be produced with a high selectivity of 33–40 mol-% and up to 75 % CO conversion, while tetragonal ZrO_2 was much less active and selective. The computational results for monoclinic ZrO_2 are in agreement with the good experimental CO conversion, as the modeled surface was found active for both H_2 dissociation and CO activation. Hydrogen was found to preferentially dissociate on the step edge, indicating that the conversion may be enhanced by the presence of such undercoordinated reaction sites. An interesting and unusual shift in the share of iso-C4 occurred after 23–112 h on stream with all catalysts: while CO conversion remained constant, the selectivity of i-C4/HC decreased, and the selectivity of methane increased correspondingly, Figure 1. We are currently studying the cause of this finding via catalyst characterization and modeling.

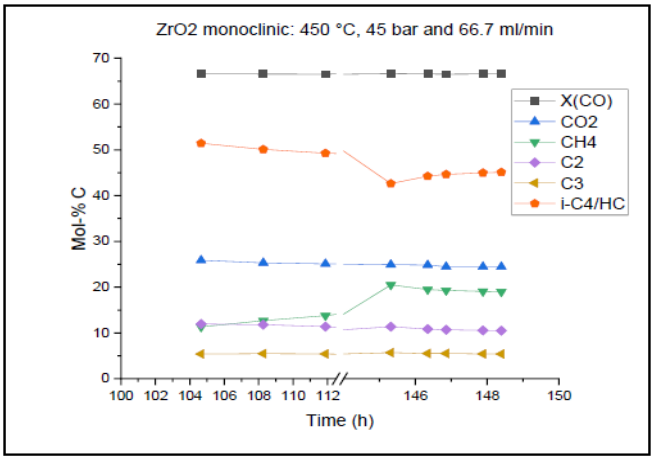

Figure 1. Catalytic performance of monoclinic ZrO_2 at 450 °C, 45 bar and GHSV = 2000 h^{-1}.

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Upgrading of Solvent-Free Acetone-Butanol Mixtures to Aviation Fuels over Heterogeneous Metal Catalysts

K. J. Betsy[1], P. Doménech[1], A. Riisager[1*]

[1]*Technical University of Denmark, Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, 2800 Kgs. Lyngby, Denmark*
**ar@kemi.dtu.dk*

Introduction. Systematically designed production of renewable transportation fuels and chemicals from the green house gas CO_2 has attracted interest in both industry and academy. Currently about 3 % of the global CO_2 emission is originating from the aviation sector by the use of fossil fuels [1]. This dependence can be diminshed by the replacement with sustainable aviation fuels (SAF) produced from CO_2 as the raw material. The strategy to upgrade fermentation mixtures from CO_2 to long-chain aliphatic ketones and alcohols (C_7-C_{11}) for liquid fuels using heterogeneous metal catalysis is attractive from the standpoint of sustainable and green chemistry but underexplored [2]. The α-alkylation of ketones with alcohols through a borrowing-hydrogen route over transition metal catalysts is an efficient methodology to obtain SAFs as water is the only liquid byproduct [3]. Use of recyclable heterogeneous catalysts is a preferred approach for the α-alkylation, and Pd nanoparticles (NPs) supported on carbon has been widely used for the reaction with moderate product yield [4]. In this study, alternative Pd-$MgSiO_2$ catalysts have been examined for upgrading of acetone/1-butanol mixtures to produce (C_7-C_{11}) ketones and alcohols under solvent free and benign reaction conditions (Figure 1).

Experimental/methodology. Catalysts with Pd NPs supported on ultra-high surface area Mg-modified silica ($MgSiO_2$) were prepared by wet impregnation and applied in batch reactions with acetone/1-butanol mixtures. With aid of various characterization techniques structure-activity correlations established.

Results and discussion. A modified Pd-$MgSiO_2$ catalyst showed 75 % conversion and high selectivity for C_7-C_{11} aliphatic ketones (78 %) under solvent free conditions at relative low temperature (150 °C). The utilization of the inherent basicity from the modified support made only a catalytic amount of base required for catalysis, and a heterogeneous behaviour without Pd leaching was found under the reaction conditions. The high surface area (> 1000 m^2/g) of the Mg-modified support not only helped to obatin a high dispersion of Pd NPs, but facilitated also synergy through strong metal-support interaction enhancing the catalysis with high selectivity for long-chain aliphatic ketones.

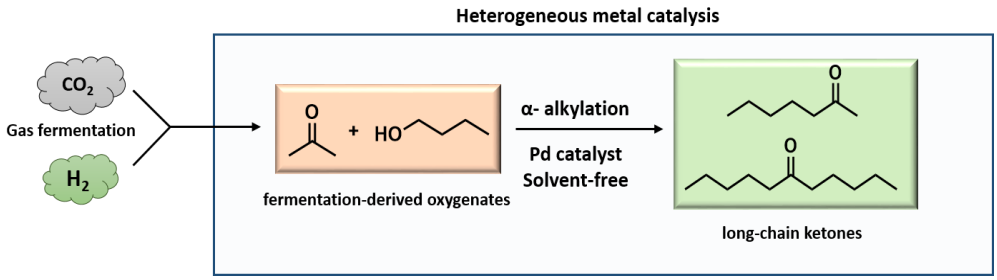

Figure 1: Schematic illustration of the synthesis of long-chain aliphatic ketones through Pd catalyzed α- alkylation

Acknowledgements
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Metal-free *N*-Doped Carbons catalysts for Solvent-Less CO_2 Fixation Reactions: A Shrimp Shell Valorization Opportunity

Daniele Polidoro,[1] Alvise Perosa,[1] Enrique Rodríguez-Castellón,[2] Patrizia Canton,[1] Lidia Castoldi,[3] Daily Rodríguez-Padrón,*[1] and Maurizio Selva[1]

[1]*Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari di Venezia, 30123 Venezia, Italy*

[2]*Department of Inorganic Chemistry, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos s/n, 29071 Málaga, Spain*

[3]*Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa 34, 20156 Milano, Italy*

*daily.rodriguez@unive.it

Keywords: metal-free *N*-doped carbons chitin chitosan shrimp shells CO_2 insertion cyclic carbonates continuous flow

Introduction. High anthropogenic CO_2 emissions are among the main causes of climate change. Herein, we investigate the use of CO_2 for the synthesis of organic cyclic carbonates on metal-free *N*-doped carbon catalysts obtained from chitosan, chitin, and shrimp shell (SSs) wastes, both in batch and in continuous flow (CF). Shrimp shells have been considered as a source of chitin suitable to synthesize *N*-doped carbonaceous materials with built-in basic properties. A procedure to convert SSs or chitin and chitosan into slightly basic solids has been coupled to the use of such materials as heterogenous catalysts for the CO_2 fixation into epoxides.

Experimental/methodology. The catalysts were characterized by a multitechnique approach and reactivity tests were run in the absence of solvents, under batch and continuous flow conditions, in the conversion of epichlorohydrin (selected as a model epoxide), into the corresponding cyclic carbonate. Also, additional batch experiments proved that the catalysts were successful on different terminal and internal epoxides.

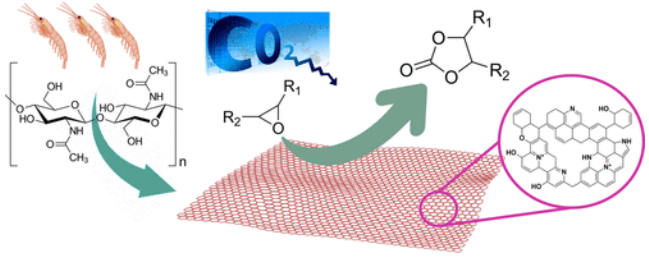

Figure 1. Schematic representation of the preparation and utilization of metal-free *N*-doped carbons.

Results and discussion. The here reported work has been aimed at achieving multiple objectives, from the design of a simple and sustainable method to obtained metal-free *N*-doped carbons to the use of such solids as catalysts for the activation and incorporation of CO_2 in the synthesis of durable chemicals/materials, and, finally, to the implementation of CO_2 cycloaddition reactions in a continuous mode to improve productivity and process intensification.[1] In particular: (i) a (small) library of catalysts with built-in basicity has been prepared from chitosan, chitin, and SS wastes through a thermal treatment carried out in the absence of additional reagents and solvents; (ii) a variety of batch experiments have demonstrated that the *N*-doped carbons, mostly those derived from chitin and SSs, were excellent catalysts for the cycloaddition of CO_2 to internal epoxides with quantitative conversion and selectivity to cyclic carbonate products up to 95–97%; and (iii) albeit investigated only for the model case of epichlorohydrin, the setup of a continuous solvent-free protocol for the CO_2 cycloaddition has confirmed that the same *N*-doped carbons allowed not only to scale-up the reaction with a productivity up to 15.0 mmol $gcat^{-1}$ h^{-1}, but they were outstandingly stable materials which did not undergo deactivation over time, at least in the explored time frame (8 h). Compared to the very recent literature of the sector, the CF procedure proved to be a robust and competitive option for the synthesis of cyclic organic carbonates.

Acknowledgments

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Effect of promoters (Cs or Ba) on the Ni/HSAG catalyzed RWGS reaction

J. Moral-Pombo[1], A. Belén Dongil[1], E. García-Bordejé[2], A. Guerrero-Ruiz[3], I. Rodríguez-Ramos[1*]
[1]*Instituto de Catálisis y Petroleoquímica (ICP-CSIC),* [2]*Instituto de Carboquímica (ICB-CSIC), Zaragoza, Spain, Madrid, Spain,* [3]*Dto. de Química Inorgánica y Química Técnica, UNED, Madrid, Spain.*
[*]*irodriguez@icp.csic.es*

Keywords: CO_2 reduction, power-to-gas, Ni metallic catalysts, Cs promoter, Ba promoter

Introduction. In order to meet the Paris Agreement, anthropogenic CO_2 emissions need to be critically diminished in a more time-consistent way. A potential solution is the so-called Power-to-Gas technology. This concept refers to the idea of storing spare electric energy as chemical energy[1]. Metallic Ni nanoparticles are among the most used catalysts for both the hydrogenation of CO_2 to methane or the reverse water gas shift (RWGS) reaction combining remarkable catalytic properties (activity and selectivity) with the fact that it is an abundant non-precious element. Understanding the role that different promoters and supports play in both the selectivity and stability of the catalyst seems to be a straightforward approach to developing efficient catalytic systems for conversion of CO_2 to CO (an intermediate for many existing processes in chemical industry such as, alcohol or Fischer-Tropsch fuels synthesis). Usually, promoters improve the catalytic performance by activating H_2 and/or CO_2, as well as increasing nickel´s reducibility and dispersion[2]. In this work, Cs and Ba have been chosen as promoters. While the first one is considered an electronic promoter, Ba has been reported to be a structural one[3].

Experimental/methodology. Catalysts were synthesized by a common incipient wetness impregnation method using nitrates as precursors. Prior to that, high-surface-area graphite (HSAG400) was chosen as support due to its open porosity and inertness which facilitates metal-promoter interaction. Activation of the catalysts was performed with hydrogen in the reactor, a U-shaped glass tube, before the catalytic tests. Outlet gases were analyzed with a Bruker CP-3380 gas chromatograph coupled with a thermal conductivity detector. Finally, the materials were studied through common characterization techniques: temperature programmed reduction, X-ray photoelectron spectrosocopy and scanning electronic microscopy, among others.

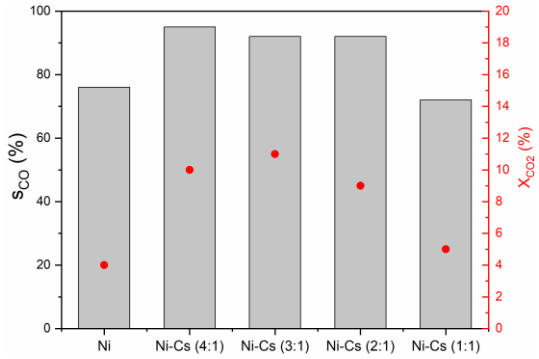

Figure 1: Catalytic performance of Ni-Cs catalysts in the CO_2 hydrogenation reaction.

Results and discussion. Kinetic regime conditions were stablished on the first place (WHSV = 36000 ml · h^{-1} · g^{-1}; H_2/CO_2 ratio = 4, granular particle size ≈ 0.25-0.35 mm). Subsequently, the catalytic properties towards CO_2 reduction of two series of promoter (Cs or Ba) Ni catalysts were analyzed and compared to the monometallic Ni/HSAG catalyst. In each series, different stoichiometric ratios between Ni and the promoter were tested. In the case of Ni-Ba catalysts, an optimal 2:1 Ni/Ba ratio allowed increasing CO_2 conversion from 4% to 15%, while selectivity towards CH_4 rose from 24% to 38%. Higher Ba-loadings resulted in lower increments of activities or selectivity values, probably due to the covering of the most suitable adsorption centers of Ni. Ni-Cs catalysts display different catalytic behavior. When catalysts are promoted using an equimolar relationship, both CO and CH_4 productions are slightly increased. The diminishment of the amount of impregnated Cs entails the complete shifting of the selectivity towards CO. A paradigmatic example of this effect can be appreciated in the case of the 4:1 Ni/Cs-containing catalyst, where s_{CO} = 95%. The conversion was also improved, producing three times more CO than our monometallic catalyst.

Acknowledgments
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Promotion of CO_2 Hydrogenation to CH_4 by MgO on Ru/ZrO_2 - Multimodal Spectroscopy Investigation

L. Santa-Taborda[1], S. Cisneros[2], L. Quintana[3], H. Abed[2], A. Ahmed[2], A. Brückner[2], A.B. Dongil[3], J. Rabeah[2], M. Romero-Sáez[1]*

[1]*Facultad de Ciencias Exactas y Aplicadas, Instituto Tecnológico Metropolitano, Medellín, Colombia*
[2]*Leibniz Institute for Catalysis (LIKAT Rostock), D-18059 Rostock, Germany*
[3]*Instituto de Catálisis y Petroleoquímica (CSIC), 28049 Madrid, Spain*
**manuelromero@itm.edu.co*

Keywords: CO_2, hydrogenation, CH_4, Ru, O-vacancies, in-situ spectroscopy

Introduction. Since metal-support electronic interactions determine the stability of key intermediates [1], efficient catalysts can be designed by the modification of electronic properties. Hydrogenation of CO_2 to CH_4 with renewable hydrogen is an attractive option for energy storage [2], yet, more efficient catalysts are still required. Therefore, a strategy such as the enhancement of defects is explored in this investigation. We demonstrate by different in-situ spectroscopic techniques how MgO incorporation in ZrO_2 boosts the CH_4 activity of Ru/ZrO_2 by changing the electronic Ru-support interactions.

Experimental/methodology. 0.4 wt.% Ru catalysts were prepared by wet impregnation over ZrO_2 and ZrO_2-MgO supports, which were prepared by precipitation and co-precipitation, respectively. The catalytic performance was determined at 1 atm at different temperatures with H_2:CO_2 ratio 4:1. In-situ EPR and dynamic in-situ DRIFT spectra were collected at similar conditions.

Results and discussion. From the catalyst screening, we found that CO_2 conversion increased by ca. 1.60 times on Ru/ZrO_2-MgO and even improved at 300 °C by ca. 1.80 times (Fig. 1a). Evidence for the involvement of paramagnetic species in the structure-reactivity behavior was provided by in-situ EPR (Fig. 1b). After reaction, a signal at g = 2.008 attributed to bicarbonate radical [3], evidenced more facile interaction between MgO-modified support and entities at the interface. Moreover, absence of Zr^{3+} signal ($g_\perp$ = 1.974) on Ru/ZrO_2-MgO suggested electron delocalization from this center probably to Ru. In-situ DRIFTS indicated that the key intermediate species (Ru-CO) was found to be less stable in presence of MgO. During a dynamic experiment, the signal 2064-2050 cm^{-1} required ca. 10 min to disappear together with that of CH_4 on Ru/ZrO_2, while for Ru/ZrO_2-MgO only 5 min were needed. Such destabilization is attributed to electron transfer from support to Ru sites. In summary, enhanced Ru-support electronic interactions induced by MgO allowed the generation of a more efficient methanation catalyst.

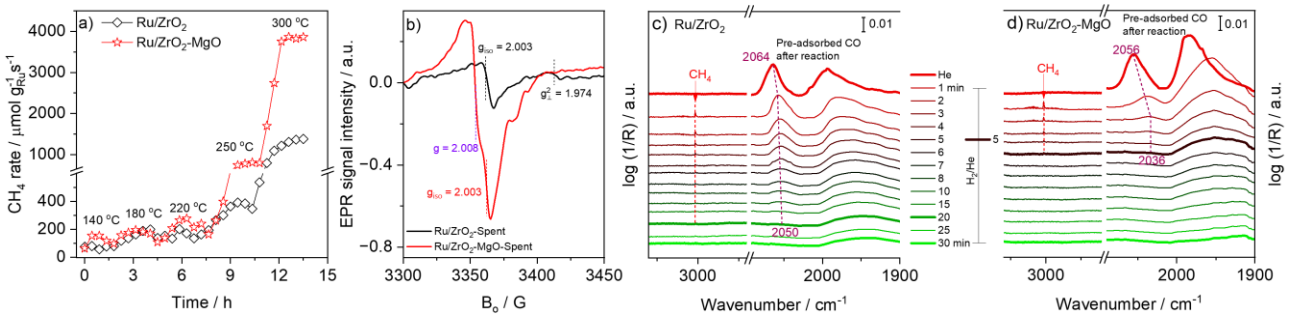

Figure 1. a) Kinetic assessments, b) in-situ EPR spectra, c-d) dynamic in-situ DRIFTS

Acknowledgments

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Evaluation of Ga and Zn-based catalysts supported on SiO_2 for the CO_2-assisted ethane dehydrogenation

H. R. Bortolini[1*], Martin Schmal[1], R. M. B. Alves[1], E. M. Assaf[2*]

[1]*Universidade de São Paulo, Escola Politécnica, Department of Chemical Engineering, São Paulo, Brazil*
[2]*Universidade de São Paulo, São Carlos Institute of Chemistry, São Carlos, Brazil*
[*]*heloisarb@usp.br; eassaf@iqsc.usp.br*

Keywords: ethane, dehydrogenation, carbon dioxide, catalysis.

Introduction. The large supply of ethane from shale gas has increased the interest on the study of its catalytic conversion to valuable products [1]. Ethane is converted to ethylene through the dehydrogenation reaction (EDH), the addition of CO_2 favors this reaction [2]. By consuming the H_2 through the reverse water gas shift reaction, CO_2 can shift the EDH reaction equilibrium leading to higher ethane conversion; in addition, CO_2 reacts with solid carbon by the reverse Boudouard reaction, producing CO and avoiding catalyst deactivation by coke deposition. In this study, catalysts with gallium (Ga) and zinc (Zn) over SiO_2 were prepared, characterized, and tested in the CO_2-assisted EDH reaction.

Experimental/methodology. The catalysts were prepared by traditional wet impregnation method over SiO_2. The samples were calcined at 600 °C for 4 hours (10 °C/min ramp) in 50 mL/min air flow to obtain the metal oxide form. The catalysts were characterized by thermogravimetric analysis, X-ray diffraction (XRD), Raman spectroscopy (pre and post reaction) and temperature-programed reduction (TPR-H_2).

The catalytic tests were performed in an automated PID Eng&Tech system in a tubular reactor with online analysis in a GC-2010 Plus chromatograph (Shimadzu) using a thermal conductivity detector (TCD) and a flame ionization detector (FID). The catalysts were tested at different temperatures and different feed gas ratios in order to identify their influence on the ethane conversion and ethylene selectivity.

Results and discussion. Catalyst characterization evidence the presence of metal oxide ZnO and β-Ga_2O_3. Both catalysts are active for the EDH reaction, as shown in Figure 1, however the gallium catalyst showed higher CO_2 conversion. In reactions with different C_2H_6/CO_2 feed ratios, both catalysts presented an increase in ethane conversion with increasing CO_2 content, indicating that CO_2 indeed assists the ethane dehydrogenation reaction. The Raman spectroscopy analysis performed after reaction identified coke deposition on the samples, suggesting possible catalytic deactivation.

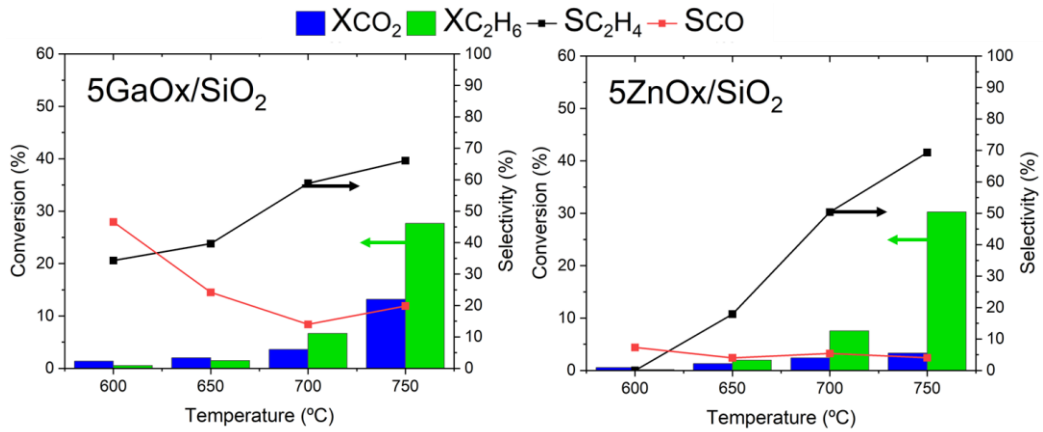

Figure 1. Temperature screening for the catalysts in the CO_2-EDH. Reaction conditions: $C_2H_6/CO_2/N_2$ = 1/1/4, total flow of 60 mL/min, WGSV = 12000 mL g^{-1} h^{-1}.

Acknowledgments

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Catalyst design, novel catalytic materials

Tuning Fe active sites in zeolites

M. Bols[1*], B. Snyder[2], D. Plessers[3], R. Schoonheydt[3], M. Dusselier[3], E. Solomon[2], B. Sels[3]

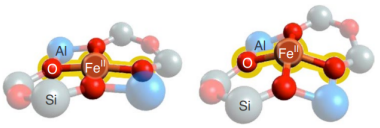
[1]*University of Ghent, Ghent, Belgium*
[2]*Stanford University, Stanford, U.S.A.*
[3]*KU Leuven, Leuven, Belgium*
[*]*maxbols@msn.com*

Keywords: spectroscopy, cage-effects, coordination chemsitry, catalysis, structure-activity relationships

Introduction. Catalytic decomposition of CH_4 and N_2O are tantalizing but fundamentally challenging goals. Current technologies based on zeolites deactivate too rapidly for practical application. We found that similar active sites hosted in different zeolite lattices can exhibit markedly different reactivity with N_2O and CH_4, depending on the size of the zeolite pore apertures and on the shape of the framework rings. These can be chosen through zeolite framework selection. The structure function relations are derived and demonstrated.

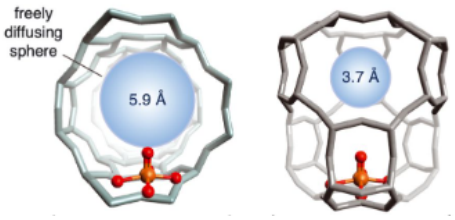
Experimental/methodology. Fe active sites were synthesised in different zeolite frameworks (BEA, ZSM-5, FER, MOR, CHA) and their reactivity with N2O and CH4 was investigated. Intermediates were identified with advanced spectroscopy (UV-Vis, FTIR, Mössbauer, NRVS, MCD, rRaman, EPR) and reaction kinetics were measured with operando UV-vis spectroscopy coupled with mass spectrometry. The results were interpreted and explained using spoctroscopically validated comutational models.

Results and discussion. Different zeolite framework have differently shaped of the 6-membered rings that host the active alpha-Fe sites.[1] This influences their ability for oxygen atom abstraction from N_2O to form highy reactive alpha-O sites.[4] The underlying property is revealed to be a geometric distortion imposed by the zeolite lattice. At the same time this disctortion influences the binding energy of the Fe ion in the exchange site,[1,3] and also the reactivity of the alpha-O site in hydrogen atom abstraction from CH_4.[2] This creates a trade-off triangle of properties steered by the 6-ring symmetry, that must be optimised to the intended application and reaction conditions.



6-membered ring shape and coordination distrorion of the alpha-Fe site

Also the window size controls reactivity of alpha-O with CH_4. Known alpha-Fe zeolite with large pore apertures deactivate completely after a single turnover. New materials with small apertures were found to regenerate 40% of active sites in zeolite after single turnover, enabling a catalytic cycle.[5] Detailed spectroscopic characterization of reaction intermediates and density functional theory calculations show that hindered diffusion through small pore apertures disfavors premature release of CH3 radicals from the active site after C-H activation, thereby promoting radi cal recombination to form methanol rather than deactivated Fe-OCH3 centers elsewhere in the lattice.



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Single-atom Ru on zeolite catalyst for the valorisation of muconic acid via isomerization and hydrogenation reactions

Ibrahim Khalil[1], Lisa De Vriendt[1], Michiel Dusselier[1*]

[1]*Center for Sustainable Catalysis and Engineering, Celestijnenlaan 200F, KU Leuven, 3000 Leuven, Belgium*

[*]*Michiel.dusselier@kuleuven.be*

Keywords: Muconic acid, metal on zeolites, heterogeneous catalysis, single-atom.

Introduction: Muconic acid (MA) can be present in 3 isomeric forms: *cis,cis* (*cc*), *cis,trans* (*ct*), and *trans,trans* (*tt*). Its added-value is attributed to its potential as a starting material for the synthesis of value-added derivatives such as **(1)** adipic acid via hydrogenation reaction, **(2)** hexenedioic acid via mono-hydrogenation, and **(3)** terephthalic acid via Diels-Alder cyclo-addition (Figure 1).[1] To access these products, the *tt*-isomer is preferred either for its stability against the intramolecular lactonization reaction or to its geometry to perform Diels-Alder cycloaddition. The biotechnological synthesis of MA produces *cc*MA and *ct*MA, thus, an isomerization step leading to *tt*-isomer must be developed. In this work, we present a single-atom Ru on Beta zeolite catalysts to investigate the isomerization of *ct*-muconates. In addition, the single-atom Ru on Beta catalysts is used for the mono-hydrogenation of MA to produce **(2)**.

Experimental/methodology: To achieve atomic dispersed Ru on Beta zeolites (12.5 < Si/Al < 250), Ru was loaded via a cation exchange method using the $Ru^{III}(NH_3)_6Cl_3$ precursor. The activation conditions were primordial to achieve both isomerization and hydrogenation activities. In that sense, the thermal dissociation of the NH_3 ligands was followed and optimized activation temperatures were found between 300 and 350°C, where only 1-2 out of the 6 NH_3 ligands remain linked to Ru (EXAFS confirmation).[2]

Results and discussion:

Isomerization: 95% selectivity towards the *tt*-isomers could be achieved together with high productivity values (up to 85 g/L.h) and TON >2500 mol/mol. In addition, deep characterization were performed (EXAFS, ICP, H_2-TPR, FT-IR, BET) to confirm the atomic distribution of Ru and elucidate the reaction mechanism. Finally, one-pot isomerization/Diels-Alder reaction was conducted to produce **(3)** after a full conversion of *ct*-muconates. This reaction was proven to be applicable to various di-alkyl muconates.

Hydrogenation: To date, the synthesis of **(2)** was only reported using electrochemical methods.[3] **(2)** can serve as a co-monomer in the synthesis of nylon-6,6 polymer, which opens routes for the functionalization of the produced polymer with chemical reactions on the C=C bonds. The difficulty in making **(2)** remain in the control of the hydrogenation step which usually end up with the formation of **(1)** after excessive hydrogenation. In this part, we present a new method to access **(2)** from MA and muconates using Ru-Beta catalysts in an H_2-free system using ethanol (solvent) as a hydrogen source. The desired product **(2)** was obtained in yields surpassing the 50% and selectivity around 70%. The optimization of the reaction conditions to achieve will be discussed in this communication.

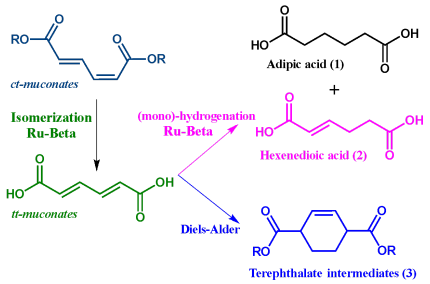

Figure 1: Reactions scheme for the isomerization of *ct*-muconates using Ru-Beta zeolites followed by the valorization of the *tt*-isomer via hydrogenation and Diels-Alder reactions.

Acknowledgments: *This work was funded by FWO foundation for postdoctoral research (grant number 1260321N for I.K.) and the Catalisti cSBO project C2O with support of VLAIO (HBC.2020.2611).*

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Hydrogen Activation on Molecular Molybdenum Sulfide Clusters Encapsulated Within the Pores of NaY Zeolites

Rachit Khare[1*], Roland Weindl[1], Christoph Gross[1], Andreas Jentys[1], Johannes A. Lercher[1]

[1]*Department of Chemistry and Catalysis Research Center, Technical University of Munich, Garching*
[*]*rachit.khare@tum.de*

Keywords: transition metal sulfides, hydrogen activation, operando spectroscopy, DFT

Introduction. Transition metal sulfides (TMS) have played an important role in industrial catalysis for over a century. Being ubiquitously utilized for heteroatom removal from petroleum feedstock, these catalysts have made their way into a multitude of other processes such as upgradation of bio-derived feedstock, reverse water gas shift reaction, CO_2 conversion, and more recently in electrocatalytic H_2 evolution. Such is the importance of these TMS phases that nature has also found a way to incorporate these active phases into its own catalysts: the enzymes. The active site in the nitrogenase enzyme, commonly referred to as the FeMo cofactor, has been identified as a Fe-Mo sulfide cluster. Industrial TMS catalysts, typically composed of sulfides of Mo or W, are often promoted with other 3d transition metals (most prominently Ni and Co). These mixed metal sulfide catalysts exceed the activity of monometallic sulfide catalysts by a wide margin. Interestingly, different mixtures of base and promotor metals result in a particular enhancement of individual reaction types. As a large fraction of reactions investigated on these TMS catalysts involve H_2 as a reactant, a significant amount of effort has been put into understanding the H_2 activation on these materials. It is widely accepted that H_2 activation on these catalysts occurs via dissociative adsorption followed by stabilization of hydrogen as either –SH groups or as hydride species. With the aim of improving the fundamental understanding the hydrogen activation in zeolite-encapsulated mixed TMS clusters, we have combined kinetic studies with *operando* spectroscopy and theoretical calculations to understand the mode of hydrogen activation on the zeolite-encapsulated TMS clusters.

Experimental/methodology. Mo was incorporated in the pores of NaY zeolite *via* chemical vapor deposition (CVD) using $Mo(CO)_6$. These precursors were sulfided at 673 K to form dimeric Mo_2S_4 species within the zeolite framework. *In situ* X-ray absorption and emission spectra (XAS/XES) were measured at P65 beamline of the German electron synchrotron (DESY) and the ID26 beamline of the European Synchrotron Radiation Facility (ESRF), respectively. DFT calculations were performed using the ORCA quantum chemistry package. All catalytic reactions were carried out in a lab-scale plug flow reactor. Ethene hydrogenation was performed at 473 K at ambient pressure with a H_2/C_2H_4 volumetric ratio of 20/1.

Results and discussion. Zeolites are ideal supports for forming well-defined TMS clusters due to their stable and structurally well-defined porous framework. We have recently synthesized homogeneously distributed molybdenum sulfide clusters encapsulated in the micropores of NaY.[1] The tetrameric Mo_4S_4 clusters structurally resemble the cubane motifs of the FeMo-cofactor and exhibited remarkable stability for ethene hydrogenation, while the classic layered MoS_2 catalyst deactivated significantly under the same conditions.[1] These promising results motivated us to address, how these clusters activate and stabilize H_2. Combining IR spectroscopy with kinetic measurements and DFT calculations we showed that the zeolite-encapsulated Mo_xS_y clusters primarily activate and stabilize hydrogen as hydride species on Mo atoms while the bulk TMS phase stabilizes hydrogen primarily as sulfhydryl (–SH) groups.[2] With the aim of further improving the molecular understanding the H_2 activation in these zeolite-encapsulated TMS clusters, we have investigated how the mode of H_2 activation varies based on their composition. Partially ion-exchanging the NaY zeolite with Ni^{2+} or Co^{2+} resulted in the formation of interconnected mixed TMS phases. Their structure was elucidated *via* a combination of XAS and DFT calculations. Further combining theory with IR spectroscopy, we could show that the S-atoms bridging the two sulfide phases provide a new site for hydrogen stabilization as –SH groups, in addition to the formation of hydride species. This additional path for hydrogen activation resulted in improved activity of these mixed TMS clusters for ethene hydrogenation.

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Activation of N_2O and CH_4 over metal-exchanged zeolite: impact of framework Al distribution

Kengo Nakamura[1], Peipei Xiao[1], Ryota Osuga[2], Junko N. Kondo[1], Atsushi Muramatsu[2], Hermann Gies[3], Toshiyuki Yokoi[1*]

[1]*Institute for Innovative Research, Tokyo Institute of Technology, Yokohama, Japan.*
[2]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan.*
[3]*Institute of Geology, Mineralogy und Geophysics, Ruhr-University Bochum, Bochum, Germany*
**yokoi@cat.res.titech.ac.jp*

Keywords: Activation of N_2O, CH_4 conversion, Zeolite, Framework Al distribution

Introduction. The use of CH_4 as the carbon source for producing value-added chemicals has attracted much attention in the last decade. The development of a catalytic process that can directly convert CH_4 into useful chemical feedstocks such as CH_3OH and C2-C4 hydrocarbons has extensively been pursuedwe report a novel catalytic process for the selective and effective production of hydrocarbons from CH_4 under mild conditions. Beside, nitrous oxide (N_2O) is a greenhouse gas and participates in the destruction of stratospheric ozone, and is also produced through NH_3 combustion process. Our strategy is based on the activation of N_2O and CH_4 over metal-exchanged zeolite to effectively produce CH_3OH, and produced CH_3OH from CH_4 is immediately converted to hydrocarbons by methanol to olefins (MTO) reaction before over-oxidation of CH_3OH. Recently, we have found that the importance of Al distribution in zeolite framework for physicochemical and catalytic properties for CH_4 activation [1]. Here, we report the design and synthesis of the zeolite catalyst enabling the production of lower olefins from CH_4 under oxidative atmosphere through the optimization of the Al distribution and the creation of both active sites for the MTM and MTO reaction in single zeolite catalyst.

Experimental/methodology. To investigate the impact of the Al distribution, aluminosilicate-type CHA zeolite with the Al distribution controlled were synthesized from different starting materials under the organic structure-directing agent (OSDA)-free conditions; the details were described in Supporting Information. Here, the CHA zeolites synthesized from amorphous silica-alumina and FAU were designated as CHA-Am and CHA-FAU, respectively. Cu species were introduced into the NH4+-form zeolites (NH^{4+}/CHA) by ion-exchange method (Cu-H/CHA-Am and Cu-H/CHA-FAU).

Results and discussion. Through various types of structural characterizations, CHA-FAU gave a significantly lower Q^4(2Al) proportion than CHA-Am, where "Q^4(*n*Al)" is $Si(OSi)_{4-n}(OAl)_n$; CHA-FAU contained more isolated Al atoms compared to CHA-Am. Catalytic conversion of CH_4 with N_2O were carried out by using Cu-H/CHA-Am and Cu-H/CHA-FAU. For both catalysts, the conversions of CH_4 and N_2O were decreased along with time on stream (TOS), while Cu-H/CHA-FAU gave a higher CH_4 conversion than Cu-H/CHA-Am. Note, there were clear differences in the products' distribution. Interestingly, for Cu-H/CHA-FAU, in addition to CH_3OH, hydrocarbons were produced. On the other hand, Cu-H/CHA-Am mainly produced CH_3OH and CO, and hardly produced the hydrocarbons. For Cu-H/CHA-FAU, the selectivity to CH_3OH was decreased but that to hydrocarbons was increased along with time on stream (TOS), suggesting that the CH_4 is converted to the hydrocarbons *via* CH_3OH and/or CH_3OH derivates. The distribution of the hydrocarbons indicats that lower hydrocarbons such as C2-C4 were selectively produced; the main products were ethylene followed by propylene. This is a typical feature of the MTO reaction over CHA-type zeolite. Hence, these results strongly suggest a new route to the production of the hydrocarbons from CH_3OH. In conclusion, we have successfully found the Al distribution greatly affected the state of the Cu species, and the catalytic performance in oxidative conversion of CH_4 and that "isolated Al atoms" would be advantageous for producing CH_3OH. In addition, the acid sites played an important role in the production of hydrocarbons; the CH_3OH produced from CH_4 is converted into hydrocarbons over the acid sites [2].

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Structure-Activity Relationships in Pt/CeO_2 Catalysts for Hydrogen Borrowing Amination

M. Douthwaite[1]*, T. Tong[1,2], L. Chen[2], R. Engel[1], M. B. Conway[1], W. Guo[2], X-P. Wu[2], X-Q Gong[2], Y. Wang[2], D. J. Morgan[1], T. Davies[1], C. J. Kiely[3], L. Chen[4], X. Liu[4], G. J. Hutchings[1].

[1]*Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Park Place, Cardiff, CF10 3AT.*
[2]*China University of Science and Technology, Shanghai, 200237, P. R. China.*
[3]*Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015, USA*
[4]*Shanghai Jiao Tong University, 200240, Shanghai, P. R. China*
[*]*Correspondance to douthwaitejm@cardiff.ac.uk*

Keywords: Transfer Hydrogenation, Hydrogen Borrowing, Green Chemistry, Amination

Introduction. Transfer hydrogenation has attracted significant attenstion since Anastas and Warner published their green chemistry guidelines back in 1998. These strategies offer alternative reaction pathways which are more atom economical than conventional methods and produce less waste. While significant research has been conducted on the use of these strategies for the hydrogenation of carbonyl compounds, their application for the production of amines is significatnly less explored. With this in mind, we set out to establish what catalytic properties might facilitate this chemistry. Pt/CeO_2 materials were used as model catalysts for this study and a reaction between cyclopentanol (CPL) and cyclopenylamine (CPA) were selected as our model reaction (**Figure 1**); dicyclpentylamine (DCPA) is produced in reaction cascade involved alcohol dehydrogenation, coupling and reduction. Importantly, hydrogen atoms generated from the dehydrogenation of CPL are utilized for the subsequent reduction of the coupled product, further improving atom efficiency.

Experimental/methodology. Several 1 *wt.*% Pt/CeO_2 catalysts were prepared by impregnation and reduced thermally to yield the final catalysts. The Pt precursor (H_2PtCl_6 or $Pt(NH_3)_4(NO_3)_2$) and CeO_2 source (Sigma Aldrich, Alfa Aesar and CeO_2 produced from $Ce(NO_3)_3.6H_2O$ decomposition) were varied to produce analagous materials, but with differing physicochemical properties. These were subsequently probed using an extensive range of characterisation methods (AC-STEM and SEM, N_2 Physisorption, CO chemisorption, CO-DRIFTS, XAS, CO_2/NH_3-TPD, INS). The catalytic performance of the materials towards hydrogen-borrowing amination was subsequently assessed in a glass batch reactor, operated under N_2.

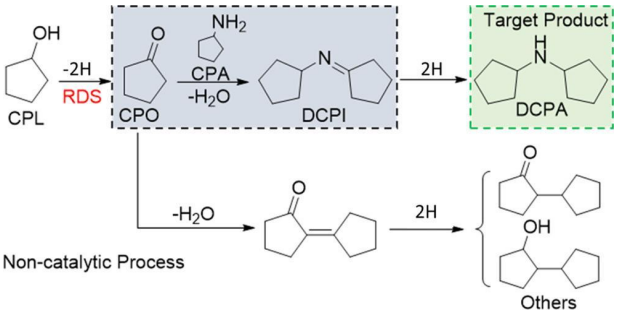

Figure 1. Schematic representation of the cascade reaction under investigation. KEY: Cyclopentanol (CPL); Cyclopentylamine (CPL); Dicylcopentylamine (DCPA); N-cyclopentylcylcopentanamine (DCPI).

Results and discussion. Both the Pt salt and the CeO_2 support used had a profound effect on the morphology of the supported Pt species. Two dimensional (2D) Pt rafts, cationic Pt species and Pt nanoparticles were all observed in these materials, but their relative quantities changed depending on the Pt precursor and CeO_2 support that was used. Importantly, the Pt morphology served as an activity indicator for alcohol dehydrogenation (rate determining). This was confirmed by subsequent density functional theorey calculations, which evidenced that the 2D Pt rafts were more effective towards alcohol dehydrogenation than the Pt nanoparticles and cationic Pt, respectively. This was supported by *quasi* in-situ INS experiments, which confirmed the existence of a Pt hydride intermediate. NH_3/CO_2-TPD experiments demonstrated that redox properties of the materials had a significant impact on the overall reaction selectivity; residual Cl^- ions were proposed to inhibit undesireable condensation reactions in favour of the desired amine, DCPA.

From Mechanism Study to Catalyst Design: Exsolved Ru Nanocatalysts on Proton Conducting Oxide for Efficient Ammonia Synthesis

H.-I. Ji[1,2*], J. Kim[1], H. Kim[1], S. Yang[1,2*]

[1] *Korea Institute of Science and Technology (KIST), Seoul, Republic of Korea*
[2] *Korea University of Science and Technology (UST) KIST Campus, Seoul, Republic of Korea*
[*] *hiji@kist.re.kr (H.-I. Ji), syang@kist.re.kr (S. Yang)*

Introduction. Since it was revealed that the ammonia synthesis reaction is associated with the nitrogen adsorption energy, represented by a volcano plot, the catalysts placed near the peak of volcano plot, particularly ruthenium (Ru), have been actively investigated [1,2]. For high efficiency of ammonia synthesis under mild conditions, the requirements of supported Ru catalysts are i) electron donating ability of supports (as promoters) that weakens the N≡N bond, ii) hydrogen absorption/desorption capability of supports to suppress H_2 poisoning on Ru surface [3], iii) refractory property for maintaining high specific surface area of supports [1], and iv) the structurally robust and uniformly distributed Ru nanoparticles [4]. However, the supported Ru catalyst that simultaneously fulfills all requirements above has yet been developed. Here we report a highly active exsolved Ru nanocatalyst supported on perovskite proton conducting oxide, $BaCe_{0.55}Zr_{0.3}Y_{0.15}O_{3-\delta}$ (BCZY), for ammonia synthesis at atmospheric pressure based on the understanding of exsolution mechanism.

Experimental/methodology. The supported catalyst, 5mol% Ru-added BCZY, $BaCe_{0.5}Zr_{0.3}Y_{0.15}Ru_{0.05}O_{3-\delta}$, was synthesized via solid state reaction using appropriate amount of oxide precursors. Analyses of XRD for crystal structure, TEM for microstructure observation, TGA for measurement of mass change against temperature, XPS for determination of oxidation state, BET for surface area measurement, and catalytic activity for quantifying ammonia synthesis rate were carried out.

Results and discussion. The exsolution is basically driven by reduction of oxide support, corresponding to the mass loss owing to the oxygen release. Thus, the decrease in mass directly associated with the Ru exsolution in a form of metal. Based on in situ TG profile at 1000°C under reducing atmosphere, it was verified that the Ru exsolution process is controlled by size-related strain, and the degree of exsolution can be effectively enhanced as the reduction time increases, e.g., from 1h to 20h. The exsolved Ru nanoparticles on proton-conducting oxide support formed by 20h reduction treatment at 1000°C had diameter of ~6 nm, and exhibited higher catalytic activity for ammonia synthesis reaction compared to exsolved Ru via 1h reduction treatment as well as the previously reported catalysts. The use of proton conducting oxide support, which has electron donating capability, structurally refractory property, and hydrogen absorption/desoprtion capability, could possibly be synergistic to boost the catalytic activity of exsolved Ru nanocatalyst. In this presentation, the details on exsolved Ru catalyst as a function of temperature, probable exsolution mechanism, and role of proton conducting oxide support will be further discussed.

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Unveiling the Evolution of N_2O Species over Atomically Dispersed Mn species supported on the TiO_2 for NOx Selective Reduction with NH_3

Yan Wang*, Sarah Komaty, Polina Lavrik, Cristina I. Q. Silva, Sudheesh Kumar Veeranmaril, Javier Ruiz-Martínez

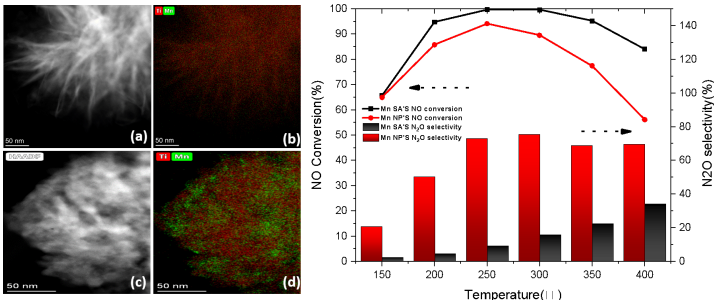
King Abdullah University of Science and Technology, KAUST Catalysis Center, Thuwal 23955, Saudi Arabia
**yan.wang@kaust.edu.sa*

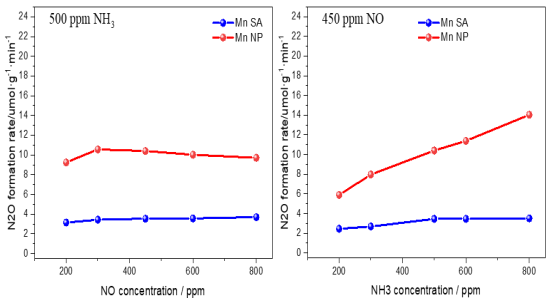
Keywords: N_2O, NH_3-SCR of NO, Mn single atom.

Introduction. Nitrogen oxides have emerged as one of the main sources of air pollution from stationary and mobile sources, which can cause serious damage to the environment and human health. Selective catalytic reduction (SCR) of NO with NH_3 has been the predominant technology for deNOx in industry. [1] To date, manganese oxides are reported to be one of the most promising catalysts for mobile source emissions at low temperatures. However, a large amount of N_2O could be produced on the MnOx in the NH_3-SCR reaction, which is the main byproduct and has a strong greenhouse effect as well as severe hazards towards human health. How to further suppress the formation of N_2O remains a challenge. Based on our previous work, we hypothesized that spacing the MnOx active sites could produce less N_2O. [2] Single-atom catalyst (SAC) has been widely used in heterogeneous catalysis due to its high dispersion and maximized atom utilization efficiency. Hence, one of the efficient approaches for clarifying N_2O species formation on MnOx-TiO_2 is to prepare single Mn-atom catalysts which by definition results in a complete dispersion and spacing of the metal over the support.

Experimental/methodology. To achieve this goal, a series of highly dispersed MnOx/TiO_2 catalysts were prepared via strong electrostatic adsorption, which was involved with anchoring Mn atom on the surface of defected-TiO_2 for different Mn loadings (1.2 to 6.0 wt.%). The sample containing Mn nanoparticles (Mn NP) with the same metal loading was prepared for comparison. The NO conversion and N_2O concentration were measured by online-FTIR and the structural properties of these catalysts were investigated by ICP, N_2-physisorption, EPR, XRD, H_2-TPR, UV-Vis, NH_3-TPD, STEM/EDX, TEM/EELS, XPS and XAS.

Results and discussion. Atomically dispersed Mn structures (Mn SA) can be confirmed using HAADF-STM and XAS whereas MnOx nanoparticles were observed in the control samples (Figure a-d). The N_2O formation rate in a wide temperature range (150-400 °C) was much lower compared to Mn NP during NH_3-SCR reaction at similar conversion ranges and at different concentrations of NH_3 and NO (Fig. e and Fig. f). Besides, more N_2O were also observed during NH_3 oxidation, NO-TPD and NH_3-TPD process, thus further verifying that atomically dispersed Mn species can suppress the N_2O formation while providing a good NOx abatement compared to samples having MnOx nanoparticles.





(e) **(f)**

Figure (a-d) HAADF-STM/EDS imaging (scan bar: 50 nm). (a), (b) is Mn SA's image; (c), (d) is Mn NP's image. (e) Catalytic performance of Mn SA and Mn NP from 150°C to 400°C. (f) N_2O formation rate of Mn SA and Mn NP at different concentrations of NH_3 and NO in NH_3-SCR reaction at 250 °C.

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Exploring the Adaptivity of Catalytic Systems in Divergent and Chemoselective Atom-Transfer Reactions

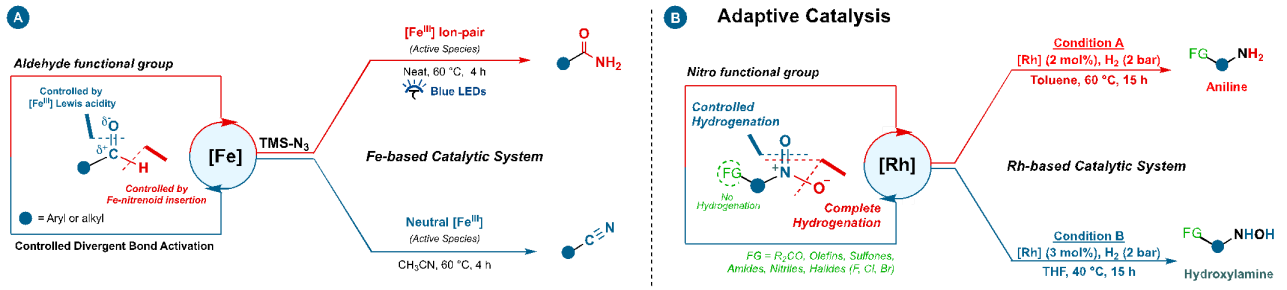
Christophe Werlé

Max Planck Institute for Chemical Energy Conversion/Ruhr University Bochum
Stiftstrasse 34 – 36 D - 45470 Mülheim an der Ruhr
christophe.werle@cec.mpg.de

Keywords: Divergent bond activation, Adaptive systems, Homogeneous Catalysis, Cooperativity

Traditionally, catalytic protocols are designed to convert substrates into a single product, preferably or even exclusively. As an alternative, the catalyst can be viewed as a system whose activity can be comprehensively adjusted by fine-tuning the reaction conditions in order to convey distinct product platforms. Such dynamic catalytic systems support the idea of molecularly controlled catalysis.[1] Understanding and designing catalytic systems in their full complexity is crucial to this approach. This can result in responsive or adaptive catalysts that enable precise control and regulation of catalytic activity. The main aim of such systems is to advance the understanding of how to control different chemical transformation sequences, ultimately producing selectively different products from a large panel of building blocks.

This lecture will provide an update on our ongoing research on the development of molecular control over bond-making and -breaking processes using adaptive transition metal systems.[2] In these systems, we demonstrate how to manipulate primary functional groups by targeting their intrinsic chemical bonds to open divergent reaction pathways. Our attention will be focused on (1) an iron-based catalyst that controls C=O versus C–H bond activation in aldehydes to open two divergent pathways and convert a wide range of substrates to the desired amides and nitriles (figure, panel A);[3] and (2) an adaptive rhodium-based catalytic system that controls the hydrogenation network of nitro-containing substrates to produce anilines and hydroxylamines (figure, panel B).[4]



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Methane oxidation on MOF Supported Fe Single-Atom Catalysts

A.M. Abdel-Mageed[1]*, B. Rungtaweevoranit[2], K.Faungnawakij[2]

1Leibniz-Institut für Katalyse (LIKAT) Rostock, Germany
[2] *National Nanotechnology Center (NANOTEC), Pathum Thani, Thailand*
*ali.abdelmageed@catalysis.de

Introduction: The synthesis of heterogeneous catalysts with well-defined active sites is essential for elucidating reaction mechanisms and further development of catalytic materials.[1] Metal-organic frameworks are excellent platforms for the achitecture of molecularly well-defined active sites.[2] This proved efficient for supporting individual metal atoms or smal metal clusters. As an example, we reported recently a Cu single-atom catalysts supported by Zr-based UiO-66 frameworks which proved highly active and stable for CO oxidation reaction.[3] Based on this approach, we expanded on our investigations to the selective oxidation of methane to methanol. Inspired by the enzyme soluble methane monooxygenase which utilizes iron-oxo species to transform methane to methanol under mild conditions,[4] we dsigned a synthetic Fe complex supported by UiO-66 framewor as an active site for this reaction.

Experimental Fe/UiO-66 catalysts were prepared by covalent attachment of Fe^{3+} ions on UiO-66 defects (see Ref.[3]). CH_4 oxidation (CH_4:O_2:H_2O = 2:1:0.2) was studied in flow-reactor at 5 bar and at T= 140-200°C. Catalysts were characterized under operando or "quasi" in-situ conditions using diffuse reflectance UV-vis, FTIR, X-ray absorption (XANS / EXAFS) , electron-paramagnetic resonance (EPR) and ^{57}Fe Mössbauer spectroscopic methods, in addition to high-resolution electron microscopy / EDS mapping.

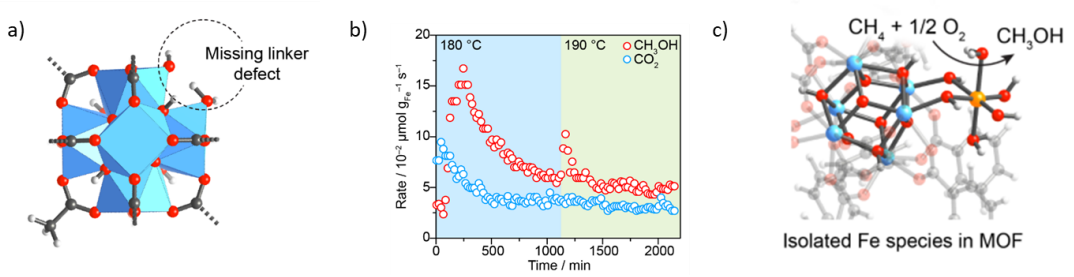

Figure1. a) Zr_6 cluster of UiO-66 with missing terephthalate linker, b) methanol and CO_2 formation rates on stream at 180°C and 190°C, c) DFT optimized strucutre of Fe-single sites where methane oxidaiton is proposed to occur.

Results and discussion: Coordination of Fe to the terephthalate defect sites (see Figure 1a) was evidenced by elemental analysis, SCXRD, PXRD and in-situ FTIR measurements. Activity measurements done at 180-190 °C indicate an initial activation phase up 250 min on-stream followed by catalyst deactivation for 500 min (Figure 1b) and reaching a steady-state production of methanol at a reaction rate of 5.9×10^{-2} µmolMeOH gFe–1 s–1 at. By monitoring the total oxidation of methane to CO_2 we estimated a selectivity for methanol and CO_2 formation under steady state of 62% and 38% respectively. The catalytic turnover for methanol formation was verified by following the rate of buildup / decay of methanol isotopomers ($^{13}CH_3OH$ and $^{12}CH_3OH$) during a transient isotope scrambling experiment using $^{12}CH_4$ and $^{13}CH_4$ isotopomers. Based on in-situ / operando spectroscopic measurements (Fe K-edge XANES / EXAFS, EPR, ^{57}Fe Mössbauer spectroscopy) and density functional theory (DFT) calculations we concluded the reaction relevant structure of Fe-active site as electron-deficient isolated Fe single sites coordinated by the UiO-66 MOF support (Figure 1c). Both the formation and depletion of these species, either by loading different Fe concnetrations or during activation/deactivation phase could be correlated with the activity of these catalysts for the selective oxidation of methane to methanol under relevant reaction conditions.

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Sub–nanometric metal species supported in MOFs for organic synthesis

Marta Mon*, Antonio Leyva-Pérez

Instituto de Tecnología Química, Universitat Politècnica de València–Consejo Superior de Investigaciones Científicas (ITQ, UPV-CSIC), Valencia, Spain
**marmoco@itq.upv.es*

Keywords: heterogeneous catalysis, MOFs, organic reactions.

Introduction. Ligand–free single metal atoms and clusters can be easily prepared in solution and catalyze relatively complex organic reactions with extremely high turnovers, >1 million in many cases, with just parts per million (ppm) of metal. This catalytic approach is very convenient for industrial purposes, where the amount of expensive metal catalysts must be minimized. Besides, if desired, the sub–nanometric metal species can be prepared in nanostructured solid materials, which allows easy recovery, reuse and implementation in continuous processes. Nanostructured solids have been traditionally used in fields somewhat away of organic synthesis, such as petrochemistry and water treatment, since spatial restrictions have been viewed as an unsurmountable issue when dealing with relatively big molecules. However, we will show here that this view can be incorrect in many cases, and that Metal-Organic Frameworks (MOFs) can be used as suitable supports for sub-nanosized metals, obtaining solid catalysts capable of carrying out complex organic reactions.[1]

Experimental/methodology. In this communication, the strategy followed to prepare and stabilize ligand–free clusters or single metal atom will be presented, which consists in the use of MOFs channels as chemical nanoreactors.

Results and discussion. Key industrial reactions such as the NH_4CN formation, CO_2 methanation, olefin hydrogenation,[2] the low-temperature water–gas shift reaction,[3] and the oxidation of alcohols[4] will be shown. Other reactions of interest in organic synthesis such the Büchner reaction,[5,6] and carbon–carbon cross–coupling reactions,[8] will be also described.

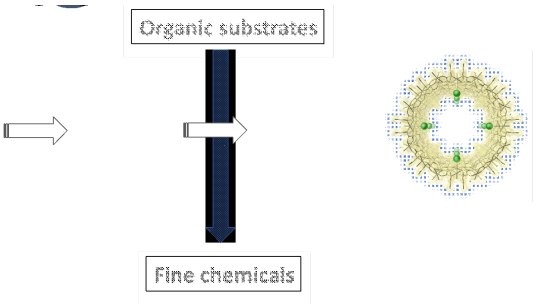

Figure 1. Ligand–free sub–nanometric metal species supported in MOFs as catalysts for organic reactions.

Acknowledgments
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Design of Metal-Organic Frameworks for Photocatalytic H_2O_2 Production

Hiromi Yamashita[1*], Yoshifumi Kondo[1], Yasutaka Kuwahara[1], Kohsuke Mori[1]

[1]*Osaka University, Suita, Japan*
[*]*yamashita@mat.eng.osaka-u.ac.jp*

Keywords: MOF Photocatalyst, H_2O_2 production,

Introduction. H_2O_2 has attracted much attention as an environmentally friendly oxidant as well as a promising liquid fuel. Photocatalytic process is a potentially sustainable method for H_2O_2 production alternative to the current anthraquinone oxidation process. Our group demonstrated that application of metal-organic framework (MOF) for photocatalytic H_2O_2 production via oxygen reduction [1]. Thanks to the advantages of the unprecedented design flexibility of MOFs, we developed the MOFs to improve the photocatalytic activity for H_2O_2 production by the linker functionalization and the missing-linker defects in the MOF framework, and the utilization of a two-phase reaction system using hydrophobic MOF [1-6].

Results and discussion. Ni/MIL-125-NH_2: Co-catalyst deposition is an efficient approach to improve photoctalytic H_2O_2 production. Ti-based MIL-125-NH_2 was synthesized using titanium isopropoxide and 2-aminoterephthalic acid and deposited with Ni nanoparticles (Ni/MiL-125-NH_2). Catalysts were dispersed in an O_2-saturated acetonitrile solution of benzylalcohol (BA) and irradiated with visible light (λ> 420 nm). Ni nanoparticles improved the selectivity for the two-electron reduction of oxygen to H_2O_2.

UiO-66-NH_2 with missing-linker: Defect engineering for MOFs is a promising process that can modulate their electronic structure, surface chemical properties and porosity. UiO-66-NH_2 consisting Zr-oxo clusters and 2-amino-terephtalate linkers was prepared and the missing-linker defects terminated by acetate ligands were introduced by adding acetic acid. Addition of missing-linker defects in UiO-66-NH_2 framework improved photocatalytic H_2O_2 production due to the promotion of linker-to-cluster charge transfer.

Two-phase reaction system with hydrophobic MOF: One critical issue of the above single-phase reaction system needs an energy-consuming separation process after the H_2O_2 production. Our group developed a two-phase reaction system, which is composed of water and benzyl alcohol, for photocatalytic H_2O_2 production utilizing hydrophobic MOF. The alkylated hydrophobic MOF was prepared by modification of the clusters in MIL-125-NH_2 with octadecylphosphonic acid (OPA). The hydrophobic MOF was dispersed in an O_2-saturated two-phase system composed of water and BA, and irradiated with visible light (λ > 420 nm). This two-phase reaction system realized spontaneous spatial separation of formed H_2O_2 to the aqueous phase and photocatalytst in BA improved the yield of H_2O_2 by preventing the H_2O_2 decomposition.

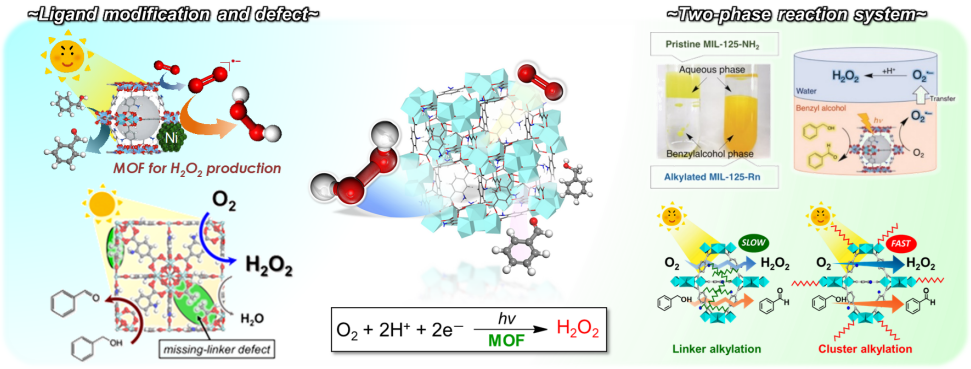

Figure 1. Design of metal-organic framework for photocatalytic hydrogen peroxide production.

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Design of oxide-polymer hybrid materials with multifunctional properties for biomass valorisation and wastewater treatment.

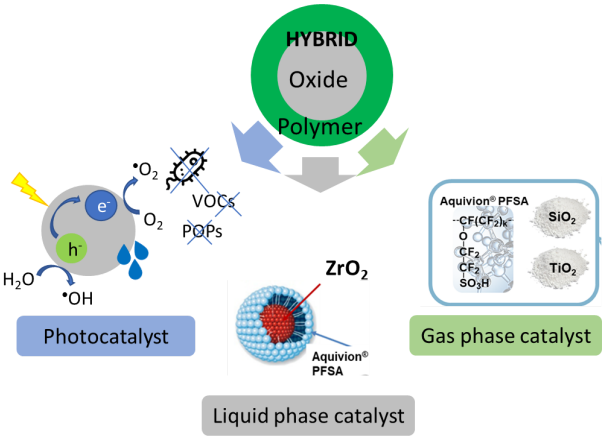
A. Allegri,[a] C. Oldani,[b] A. Brigliadori,[c] M. Blosi,[c] S. Ortelli,[c] N. Dimitratos,[a] A. L. Costa,[c] G. Paul,[d] E. Gianotti,[e] G. Fornasari,[a] S. Albonetti[a,c]

[a] *Department of Industrial Chemistry, University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy*
[b] *Solvay Specialty Polymers SpA, R&D Centre, Viale Lombardia 20, 20021 Bollate, Italy*
[c] *CNR-ISSMC (former ISTEC), Via Granarolo 64, 48018 Faenza, Italy*
[d] *Dep. of Science and Technological Innovation, Univ. of Piemonte Orientale, Alessandria, Italy*
[e] *Dep. for Sustainable Development and Ecological Transition, Univ. of Piemonte Orientale, Vercelli, Italy*
E-mail: stefania.albonetti@unibo.it

Keywords: Multifunctional catalyst, hybrid inorganic-polymeric materials,

Introduction. Multifunctional inorganic−organic hybrid materials, having both organic and inorganic components, have been recently widely investigated for their potential application in many fields. Various approaches exist for the preparation of these composites and their properties can be tuned by modification of the intimate composition. In the catalysis fields their activity is strongly correlated with the efficiency of the method of synthesis. An effective approach to develop a one-step synthesis of organic-inorganic materials with well-controlled compositions and porous textures can be the use of spray technique applied to single nanophase precursors.

Experimental/methodology. In this study, we use heterocoagulation and spray-freeze-drying (SFD) of sols containing the active phase precursors - oxides such as SiO_2, TiO_2 and ZrO_2 and polymers - to design hybrid catalysts with multifunctional properties for application in biomass valorisation and wastewater treatment.



The used synthesis process integrates colloidal heterocoagulation - exploring the electrostatic self-assembly between the oxide colloidal phase and the polymer dispersion - with the aerosol spray management and the evaporation by lyophilization.

Results and discussion. Firstly, with this procedure, nano-oxides having different Lewis acidity were encapsulated in a superacid resin matrix (Aquivion) leading to the preparation of porous micro-granules characterised by a high homogeneity in the phase distribution, high surface area and different acidity.

The presence of Brønsted sites (-SO_3H belonging to Aquivion polymer) and Lewis acid sites (belonging to inorganic supports) of the composite materials were characterized with ^{15}N isotopically labelled pyridine adsorption at 298K coupled with MAS NMR spectroscopy. The ^{15}N chemical shift of the adsorbed pyridine clearly allows to evidence the presence of Brønsted and Lewis sites and to evaluate their accessibility. The effect of acidity and of composite catalysts were studied and optimized for the gas phase dehydration of ethanol to ethylene in mild conditions [1] and for the one-pot domino reaction from furfural to γ-valerolactone. Moreover, with this procedure we coupled a microalga (*C. vulgaris*) with TiO_2 NPs exploring a new challenging frontier in the hybrid bio-nano material design [2]. Indeed, we develop a multifunction bio-nano catalyst able to combine heavy metal absorption with the photocatalytic action. With optimized synthesis we obtained a composite where TiO_2 was demonstrated to photodegrade organic compounds typical of the industrial effluents while contemporary the microalgae act as heavy metal sequestrant.

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Designing catalysts for cascade upgrading of biomass derived substrates

C. M. A. Parlett[1,2*], C.-A. H. Price[1], S. Ding[1], A.Torres-Lopez[1], C. Drivas[1]

[1]*University of Manchester, Manchester, U.K.*
[2]*Diamond Light Source, Oxfordshire, U.K.*
[*]*christopher.parlett@manchester.ac.uk*

Keywords: Catalyst design, cascade reactions, biomass valorisation, hierarchical materials, core-shell.

Introduction: Cascade reactions are sequential chemical transformations in which the starting substrate undergoes a reaction whose product becomes the substrate for the next step, and so on, until a stable product is reached.[1] Cascades offer great advantages in respect of atom economy, and time, labour and resource efficiency management, whilst permitting the use of synthetically enabling intermediates that may be impractical to isolate. However, catalytic cascades, in which the product of a reaction catalysed by species A undergoes a subsequent distinct transformation catalysed by a second species B, are hindered by the possibility of undesired interactions between the initial substrate and the second active site, or indeed between the two catalytic species. Thus highly desirable 'one-pot' catalytic cascades necessitate the spatial separation of each catalytic step. Here we report generic routes to new classes of spatially orthogonal (i.e. mutually exclusive) bifunctional porous materials,[2] comprising hierarchal bimodal porous skeletons and porous core-shell architectures, both enabling the chemical environment of distinct pore regions to be independently tuned. The hierarchical nature of the pore networks, either bimodal or core-shell, regulates active site accessibility and communication between different spatially localised catalytic functionalities.

Experimental: Hierarchical porous architectures have been synthesised via either duel templating strategies or desilication of commercial microporous zeolites, while porous core-shell structures are produced by consecutive growth strategy employing a bi-phasic synthesis protocol. Controlled active site deposition, through either blocking of locations by pore templates or capping agents or through size limitations, allows for the coupling of complementary sites, including two distinct metal nanoparticles (NPs), an acid and a base, and an acid and metal NPs. These configurations are tuned for one-pot alcohol selective oxidation, transesterification and esterification, and hydrodeoxygenation (HDO) cascades.

Results and discussion: Spatial compartmentalisation of 2.4 nm Pt NPs and 5.5 nm Pd NPs within mesopores and macropores of a bimodal porous silica,[2] was verified by HAADF-STEM imaging (Fig. 1), electron tomography, and simultaneous surface (SEM) and bulk (DF-STEM) imaging. The subsequent material displays the catalytic advantage of spatially segregating Pt NPs within mesopores, accessible only through interconnected Pd containing macropores, for the cascade selective oxidation of cinnamyl alcohol → cinnamaldehyde → cinnamic acid (Fig. 1). Catalytic Biofuel production, via the combined transesterification and esterification, has been facilitated by the spatial separation of $Zr(SO_4)_2$ (acid), in macropores, and MgO (base), within mesopores, akin to the selective oxidation system.[3] In a similar fashion, Pd doped in mesopores and acid sites in micropores of hierarchical porous zeolite has shown excellent HDO performance for the cascade reduction → dehydration → hydrogenation of fatty acids into alkanes. Core-shell structures have also been developed for biofuels, via consecutive dehydration and hydrogenation, for the conversion of fructose into biofuels over acid and metal NP sites, respectively.

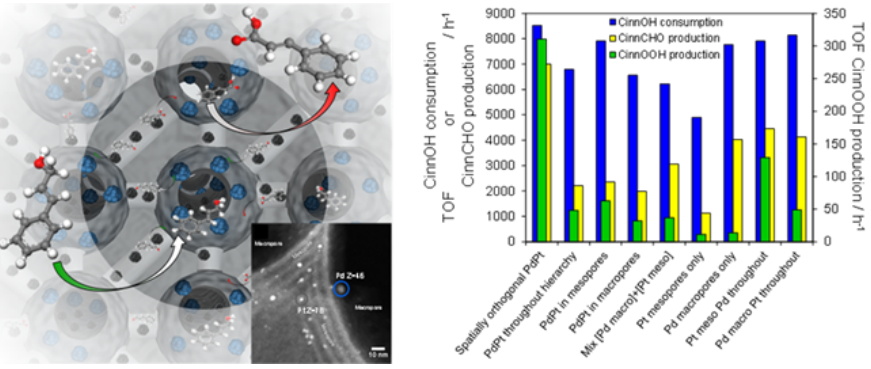

Figure 1. (left) Concept of spatially orthogonal selective oxidation catalysts, with inset HAADF-STEM image. (right) Catalytic cascade selective oxidation of cinnamyl alcohol.

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Iron based composite catalyst for magnetically-induced hydrogenation reactions in gas and solution phase

S. Ghosh[1*], T. Ourlin[1], J. Mazario[1], S. Cayez[1], S. Daccache[1], J. Carrey[1], B. Chaudret[1*]

[1]*LPCNO (Laboratoire de Physique et Chimie des Nano-Objets), Université de Toulouse, CNRS, INSA, UPS, 31077 Toulouse, France.*

[*]*ghosh@insa-toulouse.fr, chaudret@insa-toulouse.fr*

Keywords: Sabatier reaction, Magentically-induced catalysis, Eddy current

Introduction. Recently, magnetically induced catalytic CO_2 hydrogenation has gained lots of attention due to its high energy efficiency and better heat management of exothermic processes as compared to thermal heating.[1] In particular, ferromagnetic nanoparticles (dual heating and catalytic agent) are shown to be active for this process, but the complex synthesis of such nanoparticles hinders their potential to be a commercial success.[2] Herein, a single macroscopic Fe based (SiO_2 and Ni coated) composite with dual functionality was realized and tested for magnetically induced gas-phase methanation and further proved to be active for the liquid phase model hydrogenation and hydrodeoxygenation reactions.

Experimental/methodology. The SiO_2 coating of the Fe wool was carried out using a simple sol-gel chemistry route involving hydrolysis and polycondensation of TEOS, followed by annealing. Subsequently, the Ni deposition was accomplished using an organometallic decomposition route in presence of the Fe wool and the Fe wool@SiO_2 (Fig. 1). All as-prepared samples were characterized using XRD, ICP-AES, VSM, SAR, XPS, SEM, SEM-EDS elemental mapping, and FIB-SEM techniques. The continuous gas phase CO_2 methanation was carried out in fixed bed reactor and liquid phase catalytic reaction in batch type reactor.

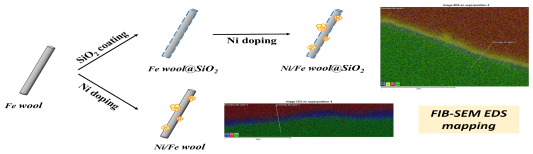

Figure 1. a) Schematic representation of Fe wool functionalization and the respective FIB-SEM EDS mappings.

Results and discussion. The enhanced catalytic activity (higher CO_2 conversion and CH_4 selectivity) of Ni deposited silica coated Fe wool as compared to the uncoated counterpart could be attributed to the presence of SiO_2 layers, providing more stability to the surface Ni species (Fig. 2a,b). An addition of a Siralox filler in the catalytic bed further improves the CO_2 conversion and CH_4 selectivity, and the stability of the catalyst (30 h on stream). Furthermore, this composite catalyst was demonstrated to be active for solution-phase model hydrogenation (styrene and nitrobenzene) and hydrodeoxygenation (acetophenone and diphenyl ether) reactions with 5mol% Ni loading (Fig. 2c). Herein, the combined XPS, FIB-SEM, and SAR measurements, signifies the judicious choice of SiO_2 coating and the utilization of eddy current mediated heating of Fe wool for the development of stable, energy efficicent, and inexpensive Fe based catalyst.

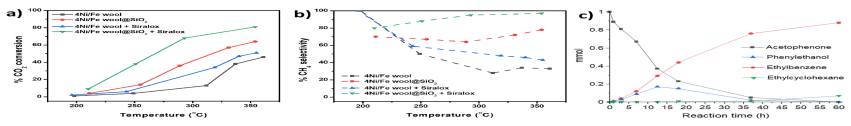

Figure 2. Plot of a) %CO_2 conversion as a function of temperature, and b) CH_4 selectivity as a function of temperature, c) solution phase kinetic data for acetophenone hydrodeoxygenation reaction using 4Ni/Fe wool@SiO_2 as a catalyst.

Acknowledgments

Authors gratefully acknowledge the funding from the ERC Advance grant (MONACAT 2015-694159).

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Liquid Metal Boosting Stability of Methanol to Hydrocarbons Conversion

Yong Zhou[1], Mariya Shamzhy[2], Maya Marinova[3], Pardis Simon[1], Andrei Y. Khodakov[1],*
Vitaly V. Ordomsky[1]*

[1]*Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 – UCCS, F-59000, Lille, France*
[2]*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 2030/8, 12843, Prague, Czech Republic*
[3]*Institut Michel-Eugène Chevreul, 59655 Villeneuve-d'Ascq, France*
**Andrei.Khodakov@univ-lille.fr, Vitaly.Ordomsky@univ-lille.fr*

Keywords: Methanol-to-hydrocarbon, catalytic stability, zeolite, liquid metal, gallium

Introduction. Methanol-to-hydrocarbons (MTH) has been considered as one of the most practical approaches for producing high-valuable products.[1] However, the commonly used zeolite catalysts suffer from rapid deactivation due to coke deposition and require regular regeneration treatments. Inspired by the versatile roles of liquid metal for promoting the supported metal catalysts,[2] we demonstrate that the low-melting-point liquid metal can effectively promote more stable methanol conversion in MTH process by modifying acid sites of zeolite and accelerating the desorption of bulky products from zeolite surface. The ZSM-5 zeolite promoted with the liquid metal of gallium exhibited a more stable MTH lifetime of 32 h than the ZSM-5 alone (8 h) at the same conditions.

Experimental/methodology. HZSM-5 catalysts were prepared via calcination of NH_4-ZSM-5 (Zeolyst, CBV2314, SiO_2/Al_2O_3~23). The reference Ga_2O_3/ZSM-5 with a nominal 10% wt. Ga loading was prepared via incipient wetness impregnation. Ga/ZSM-5 was obtained by treating the HZSM-5 with metallic Ga (Sigma-Aldrich) under N_2 at 200 ^{0}C with subsequent separation of zeolite. Ga+ZSM-5 is physically mixed HZSM-5 with Ga. The MTH reaction was performed in a fixed bed quartz tube reactor at 400 ^{o}C at atmospheric pressure using N_2 flow saturated by methanol with GC analysis at the exit of the reactor.

Results and discussion. We have discovered that the MTH catalytic stability of ZSM-5 catalyst containing liquid metal Ga outperforms the ZSM-5 zeolite and Ga_2O_3-supported catalyst (**Figure**). Multiple characterizations of FTIR, TEM, XPS, TG and N_2 adsorption revealed that the liquid metal penetrates the pores of zeolite, interacts with acid sites and it favours the desorption of bulky molecules from the pores (**Figure**). It results in the suppression of coke formation and an increase in the stability of the catalyst 4 times from 8 to 32 h.

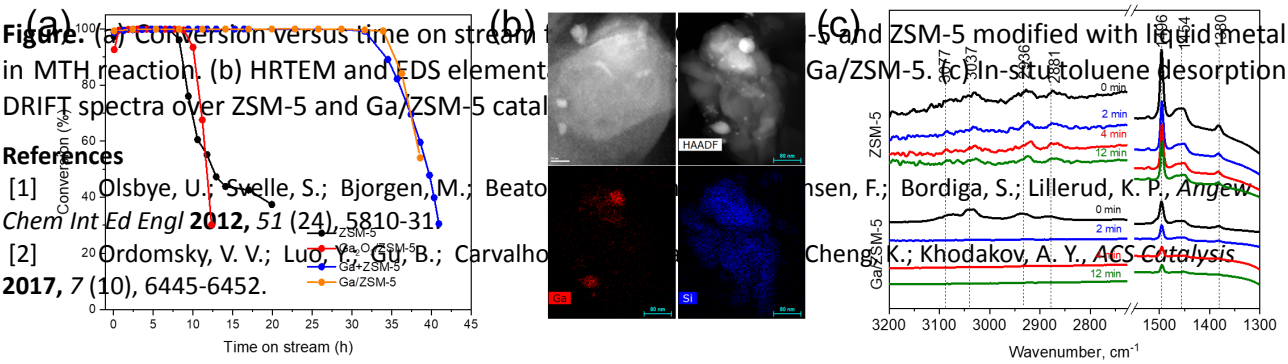

Figure. (a) Conversion versus time on stream f -5 and ZSM-5 modified with liquid metal in MTH reaction, (b) HRTEM and EDS element Ga/ZSM-5. (c) In-situ toluene desorption DRIFT spectra over ZSM-5 and Ga/ZSM-5 catal

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Perovskites as High Performance reverse Water Gas Shift Catalysts

L. Lindenthal[1], F. Schrenk[1], H. Drexler[1], T. Berger[1], R. Rameshan[1], T. Ruh[1], T. Cotter[1], C. Rameshan[1]*

[1]*Chair of Physical Chemistry, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria*
christoph.rameshan@unileoben.ac.at

Keywords: perovskite, rWGS, exsolution, doping, catalysis, high temperature

Introduction.

The utilization of CO_2 in chemical reactions could potentially provide a way to alleviate the impact of the industrial sector on climate change. As shown in previous works, perovskite type oxides (general formula ABO_3) have great properties to be used as catalysts for reactions – particularly the reverse water gas shift reaction (rWGS) – that mitigate CO_2 emission of the industrial sector [1]. The reason is the thermal stability of perovskites even under harsh reaction conditions and high T and their beneficial surface reactivity.

Experimental/methodology.

In this study we investigated the effects A- and B-site doping of the host latice on exsolution properties, oxygen surface chemistry and the corrsponding catalytic activity. Therefore, multiple series of catalysts were prepared utilizing a modified pechini synthesis route. The B-site undoped series $M_{0.6}Ca_{0.4}FeO_{3-\delta}$ (M = La, Nd, Pr) was compared to a series where the catalytically active metal X was doped on the B-site $M_{0.6}Ca_{0.4}Fe_{0.9}X_{0.1}O_{3-\delta}$ (X = Co, Ni). To obtain operando data on structural changes synchrotron based X-Ray Diffraction was applied. Additionally, to better understand the role of the A-site elements, Density Functional Theory (DFT) calculations were performed.

Results and discussion.

Catalytic results pictured in Figure 1 show that the Pr based perovskite is the most active one among the A-site variations. In total the activity of the catalyst could be doubled by the change of the A-site element from La to Pr. Also, in comparison to the Nd based catalyst the activity was increased by around 66 %. This different behavior can be explained by the different size of the exsolved nanoparticles and the modified surface chemistry of the host lattice, both observed by operando XRD. Altogether we could show that an increased redox activity of the A-site can be linked directly to improved redox chemistry of the surface which leads to better catalytic rWGS performance (i.e. the concentration of surface vacancies for CO_2 activation). Additionally, the variation of the B-site doping can further improve the catalytic performance.

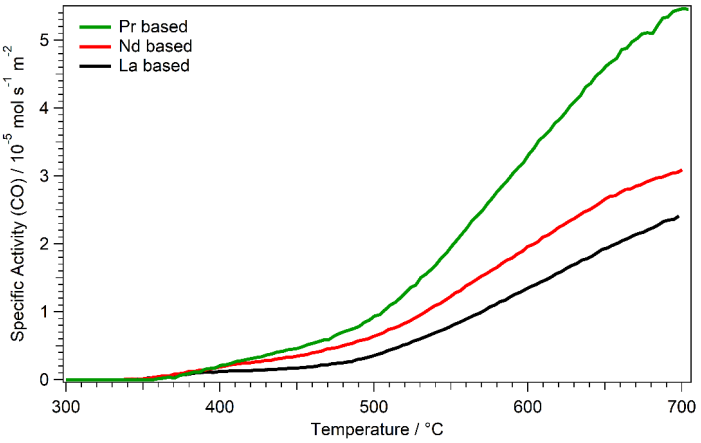

Figure 1: Comparison of the catalytic rWGS tests of Co-doped perovskites with different A-site cations for increased surface reactivity. The Pr based catalyst proved to be the most active, followed by the Nd and La based.

Acknowledgments

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement n° 755744 / ERC - Starting Grant TUCAS).

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Towards efficient water oxidation catalysis using ruthenium coordination oligomers anchored through CH-π interactions

M. Gil-Sepulcre,[1,2] O. Rüdiger,[2] S. DeBeer,[2] A.Llobet[1,*]

[1] *Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology (BIST), Tarragona, Spain*

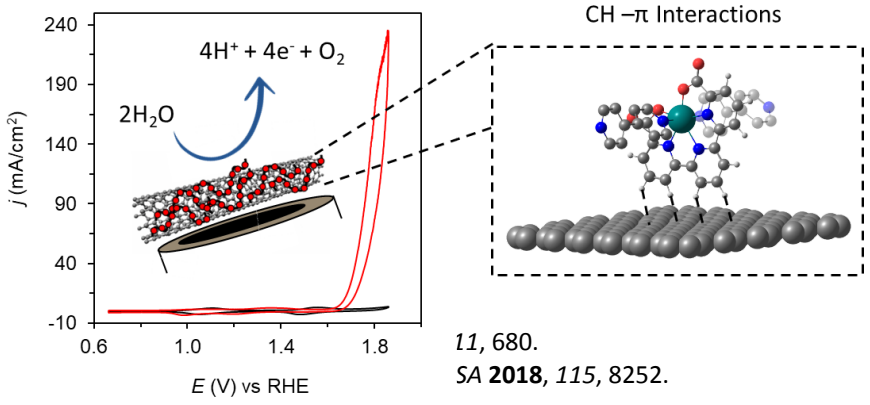
[2] *Max Planck Institute for Chemical Energy Conversion, 45470 Mülheim an der Ruhr, Germany*

[*] allobet@iciq.es

Keywords: Water Oxidation, Solar Fuels, Redox Catalysis, Molecular Anodes

The search for environmentally benign renewable energy sources as alternatives to the combustion of fossil fuels is a key target considering the continuously increasing energy demands and the consequences of the associated greenhouse gas emissions.[1],[2] Within this context, artificial photosynthesis is one of the most promising solutions. In particular, water splitting with sunlight (h*v*-WS), where sunlight drives the water oxidation to dioxygen (WO) and proton reduction (PR) to hydrogen is the most promising approach.[3] To achieve the design of an efficient and robust artificial device, a catalyst is needed for both processes.

Here, we show a new family of Ru-based oligomeric catalysts that can be anchored on the surfaces of graphitic materials through CH-π interactions between the auxiliary ligands bonded to Ru center and the hexagonal rings of the graphitic surfaces. A combination of spectroscopic, microscopic and electrochemical techniques allows an exquisite molecular control of the catalytic process. The resulting hybrid materials achieved current densities in the range of 0.2-0.3 A/cm^2 at neutral pH values, and remarkable long-term stabilities for more than 12 hours towards oxidation of water to dioxygen.[4],[5]



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Metal Nanoparticles Immobilized on Functional Supports: Toward Adaptive Catalytic Systems

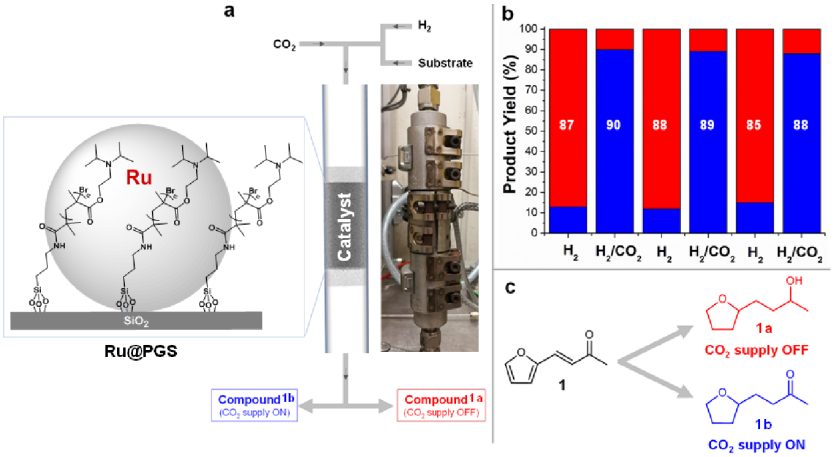
A. Bordet[1*], W. Leitner[1,2]

[1]*Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany*
[2]*Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany*
[*]*alexis.bordet@cec.mpg.de*

Introduction. Chemical transformations with molecular hydrogen (H_2) are fundamental pillars of the chemical industry and used across the whole value chain ranging from the production of fuels, fine chemicals, agrochemicals, and pharmaceuticals. Catalysts are essential to control the activation and transfer of hydrogen in particular for the selective conversion of biomass-derived substrates and intermediates. In this context, we have shown that the use of molecularly modified surfaces (MMS) as matrix for the synthesis and stabilization of metal nanoparticles is a versatile strategy to produce multifunctional NPs@MMS catalysts with tailor-made reactivity.[1] While these previously developed catalysts present often outstanding properties regarding their dedicated tasks, their performance is typically optimized to remain static. In a world where flexibility is becoming increasingly important, the design and development of adaptive catalysts - referring here to catalytic systems whose reactivity is reversibly modified upon changes in the reactive environment - is of great interest, but remains difficult.

Experimental/methodology. To tackle this challenge, a multifunctional hydrogenation catalyst composed of ruthenium nanoparticles immobilized on an amine-functionalized polymer-grafted silica (Ru@PGS, Figure 1) was prepared.

Results and discussion. Using the hydrogenation of biomass-derived furfuralacetone (**1**) as model reaction, we show that when the hydrogenation was performed under pure H_2, **1** was completely hydrogenated to give the corresponding saturated alcohol (**1a**). However, when a mixture of H_2 and CO_2 was used, a sharp change in selectivity was observed, and the ketone was conserved (product **1b**). The change in selectivity – which was not observed for a reference Ru@SiO_2 – is presumably due to the formation of alkylammonium formate species coming from the reaction between the amine functionality, CO_2 and H_2. This process is reversible, allowing switching the feed gas composition back and forth between H_2 and CO_2 + H_2 in continuous flow reactor to produce either the saturated alcohol **1a** or the saturated ketone **1b** in excellent selectivities and yields (Figure 1b-c).[2] This successful example of real-time selectivity switch shows how the combination of functional supports and metal NPs provides a versatile molecular approach to design and produce multifunctional catalytic systems with adaptive reactivity. Further examples and extension of this concept will be reported,[3] including other approaches to real-time and reversible switching of catalyst performance such as magnetically induced local heating.[4-5]



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Hetero-Bio Catalytic Systems for Redox Reactions

T. Sudmeier [a], K.A. Vincent,[a] S. Freakley[b]

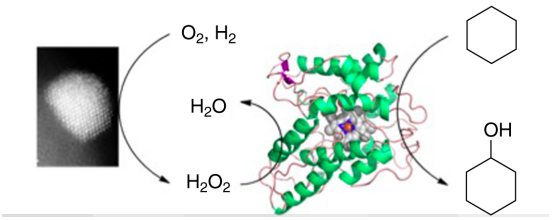
[a] *Inorganic Chemistry Laboratory, South Parks Rd, OX1 3QR, Oxford*

[b] *Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY*

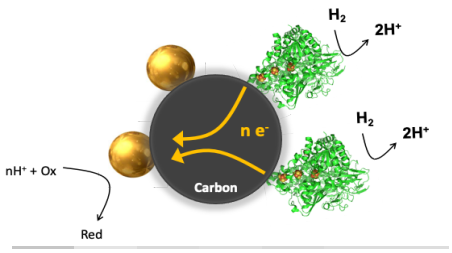
[*] *sf756@bath.ac.uk*

Introduction. Developing catalytic systems that combine the benefits of both heterogeneous and biocatalysts allows new approaches to perform highly selective oxidation and hydrogenation reactions. These approaches to combining catalytic systems can allow high regioselectivity, reaction at mild conditions and increased atom efficiency by removing sacrificial reagents or co-factor regeneration steps. Connecting these two different fields of catalysis can be achieved by either i) a tandem cascade system – where reactions happen independently on each type of catalyst at matched rates (Figure 1) or ii) a cooperative mechanism where both catalytic sites are electronically connected to provide sites of complimentary redox half reactions (Figure 2). This contribution will describe our progress in developing tandem systems which utilise *in situ* produced H_2O_2 and peroxygenase enzymes for selective C-H/C=C oxidaiton at mild conditions [1,2] and cooperative hydrogenase / metal nanoparticles systems for selective hydrogenation at conditions where traditional precious metal catalysts (Pd/C) become inactive.

Experimental/methodology – Heterogeneous catalysts were prepared by previously reported impregnation methods [2] or purchased commercially (e.g Pd/C). Bio-heterocatalytic tests were typically carried out in aqueous phosphate buffered solutions pH 6-8, with low gas pressures (1-3 bar) and substrate concentration 1- 10 mM in stirred glass reactor systems. Analysis was carried out by GC-MS and NMR methods.



Results and Discussion. *C-H Activation* – Continuous low-level supply or *in situ* generation of H_2O_2 is essential for the stability of unspecific peroxygenases, which are deemed ideal biocatalysts for the selective activation of C–H bonds. To envisage potential large-scale applications of combined catalytic systems the reactions need to be simple, efficient and produce minimal by-products. We show that gold-palladium nanoparticles supported on TiO_2 or carbon have sufficient activity at ambient temperature and pressure to generate H_2O_2 from H_2 and O_2 and supply the engineered unspecific heme-thiolate peroxygenase PaDa-I. This tandem catalyst combination facilitates efficient oxidation of a range of C-H bonds to hydroxylated products in one reaction vessel with high selectivity including substrates such as cyclohexane, ethylbenzene, tetralin, and styrene.



***Selective Hydrogenation* -** Here, we explore a new concept in catalytic hydrogenation by combining bio- and heterogeneous chemo-catalysts containing cooperative active sites electronically connected via a conductive carbon support. More specifically, we show how co-immobilising a hydrogenase enzyme with palladium nanoparticles on a carbon support leads to a significant rate enhancement in the hydrogenation of model alkynes. The effect is observed in different pH regimes and buffer systems. On top of increasing the rate, the presence of a hydrogenase was shown to alleviate substrate poisoning of the palladium catalyst and lead to a different product distribution. In this work we demonstrate the benefits of electronically coupling enzymatic active sites to a heterogenous chemo-catalyst via a carbon support to facilitate hydrogenation reactions under low hydrogen pressures.

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Exploring the wide experimental parameters space: low temperature, sustainable and rational wet-chemistry approaches to heterogeneous catalysts

Silvia Gross[1,2*]

[1] *Dipartimento di Scienze Chimiche (DiSC), Universita` degli Studi di Padova (UniPD), via Marzolo, 1, 35131, Padova, Italy*
[2] *Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Engesserstraße 20, 76131 Karlsruhe, Germany*

[*]*Corresponding Author's E-mail address silvia.gross@unipd.it*

Introduction.
Targeting the increase of activity and selectivity, the reduction in the use of critical raw materials and precious metals, the reduction of the water and carbon footprint of the catalyst production routes requires the exploration of novel catalyst morphologies[1] as well as the optimisation of more sustainable and rational synthesis approaches allowing size, shape and composition tuning.
In this talk, a broad toolbox[2,3] of different wet chemistry and colloidal routes to inorganic systems for heterogeneous catalysis will be presented, which are pooled by low or even room temperature of exercise and processing, use of water or other not harmful solvents, ease of implementation, high yields and polymorphs selectivity, high reprodicibility and potential scalability. Highly controlled synthesis of metal and metal sulphide/oxides nanoparticles, pure and doped oxide supports, supported catalysis can be pursued by these approaches. The exploration of the broad experimental parameters space can be profitably supported by rational approaches such as Design of Experiment[4], dramatically reducing time, raw materials and energy consumption. Examples of application of the prepared heterogeneous catalysts to photocatalysis and emission control catalysis will be presented.

Acknowledgments.
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Synthesis of high-entropy oxides for catalytic applications

A. J. Knorpp[1*], M. Stuer[1]
[1]*Empa High-performance ceramics laboratory, Duebendorf, Switzerland*
[*]*Corresponding amy.knorpp@empa.ch*

Keywords: High-entropy oxides, high-entropy hydroxocarbonates, synthesis, Layered double hydroxide

Introduction

High-entropy materials (HEMs) are an emerging field that has expanded well beyond their origins in metal alloys and now include the materials like oxides[1] and carbides[2]. The driving concept for high-entropy materials is similar across all material classes, where the incorporation of multiple elements, their equimolar concentration, and their homogeneous distribution in the structure maximize configurational entropy. High-entropy oxides (HEOs), a subcategory of high-entropy ceramics, are becoming an enticing materials platform for a wide range of applications including catalysis, because of increased stability and unexpected properties arising from lattice distortions and cocktail effects between multiple cations.

Despite the recent interest in HEOs for catalysis,[3,4] HEOs are primarily synthesized by solid-state methods, where there is little control over morphology, porosity, and particle size.[5] As the field of high-entropy oxides is expanding into a wide range of applications like catalysis, synthesis strategies that can control its physical properties are needed.

Experimental/methodology.

Different synthesis strategies (hydrothermal and co-precipitation) have been utilized to adapt hydroxocarbonate structures to high-entropy forms, where systematic syntheses for chemistry containing 5 or more cations have been preformed. Special attention is given to cations that have particular interest for catalysis with varying combinations of Al, Mg, Cr, Fe, Co, Zn, Cu, Ni, Ga, In, Y, Ho, Er, Ce, and La cations. This material then serves as a precursor to high-entropy oxides when calcined.

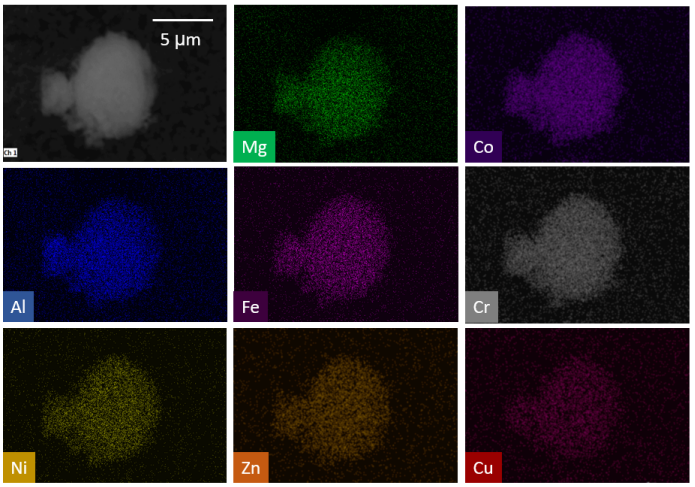

Figure 1: SEM micrograph of high-entropy layered double hydroxide

Results and discussion.

The chemistry of high-entropy precursor materials can be tailored by selecting a wide range of cations and cations sizes, and satisfies the criteria for high-entropy classification with 5 or more cations that are homogenously distributed in the structure (Figure 1).[6] High-entropy precursors are then calcined to a high-entropy spinel or rock salt oxide structure and maintain the chemistry, morphology, as well as, some porosity from their high-entropy precursors.

The expansion of high-entropy materials to include tailorable high-entropy precursors is an important step in the development of these materials' use in catalytic applications, thanks to their porosity as well as tailorable surface and bulk chemistry.

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Tailoring metal-support interactions via pseudo single-atom inverse catalyst system

Lebohang Macheli[1,3], Gerard Leteba[1], Bryan Doyle[2], Linda Jewell[3], Eric van Steen[1]

[1]*Catalysis Institute, Department of Chemical Engineering, University of Cape Town, Private Bag X3, Rondebosch 7701, South Africa*
[2]*Department of Physics, University of Johannesburg, PO Box 524, Auckland Park 2006, South Africa*
[3]*Department of Chemical Engineering, University of South Africa, Florida Campus, Johannesburg 1710, South Africa*

Introduction. The cobalt-catalysed Fischer-Tropsch synthesis typifies a conversion-efficient chemical process for the synthesis of liquid hydrocarbons from CO. However, the traditional Fischer-Tropsch synthesis is subjected to selectivity limitations for the major products[1]. Here we illustrate that almost atomically dispersed of SiO_x-moieties on the surface Co nanoparticles creates a SiO_x-Co interface which enhances activity in the Fischer-Tropsch and leads to chemical properties that tune the selectivity in favour of paraffins. Most of all, the inevitable by-production of methane is impeded resulting in a minimal amount of methane (< 4%). Moreover, this modification makes best use of cobalt and increase the turnover frequency (TOF). Such an increase in the TOF may provide the viability of practical applications of these catalytic systems in industry.

Results and discussion. Pseudo atomic deposition of silicon on cobalt oxide was performed by contacting cobalt oxide with trimethylchlorosilane (TMCS) in n-hexane at room temperature, followed by calcination at 873K yielding Si modified cobalt oxide. The resulting material was characterized using SEM-EDX, TEM, XRD, TPR, XPS, Raman spectroscopy, and FT-IR. SEM-EXD indicates the homogeneous dispersion of silicon over the oxide surface. Both FTIR and XPS suggest the dispersion of mononuclear Si surface species. Raman spectroscopy shows a low relative intensity of the silicate-sensitive peak which is indicative of the low degree formation of SiO_2 on the Co_3O_4 nanoparticles presumably due to low concentrations of SiO_x moieties. We show that metal-oxide interface improves the catalytic activity and selectivity of the catalyst in the Fischer-Tropsch synthesis. Turnover frequency (TOF) increases by over 10 folds upon incorporation of SiO_x on the cobalt surface. This change is due to electronic modifications at the SiO_x-Co interface which increases the heats of CO adsorption. The change on heat of adsorption favors the dissociation on CO as seen by the increase in the intensity of the high temperature CO-TPD peak.

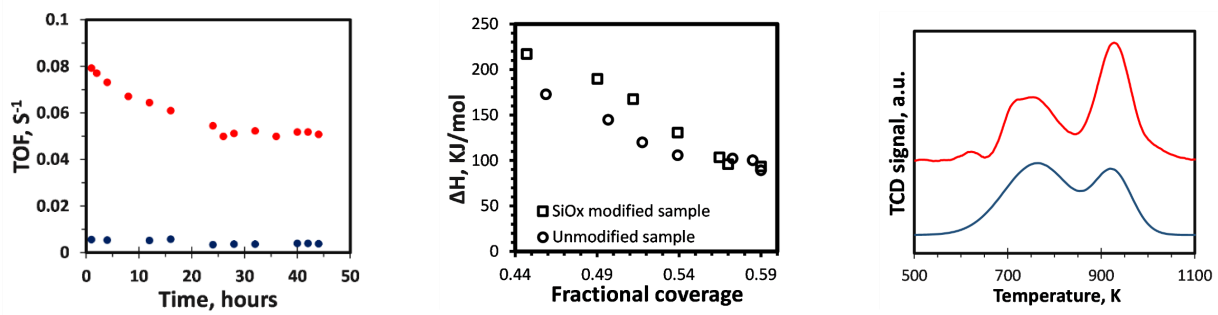

Figure 1: Effects of SiO_x-Co interface on a) catalytic activity of cobalt TOF as a fuction of time b) change of heat of adsorption of CO with fractional CO coverage and c) CO-TPD profile (red line- modified, blue line – sample)

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$ZnFe_{2-x}Rh_xO_4$ mixed metal oxides as catalyst precursors in C1 chemistry

D. Delgado[1], G. Koch[1], S. Jiang[1], J. Kröhnert[1], X. Q. Tran[1], F. Schmidt[1], T. Lunkenbein[1], C. Galdeano Ruano[2], J. Gaona-Miguélez[2], R. Schlögl[1], P. Oña-Burgos[2*], A. Trunschke[1*]

[1]*Fritz Haber Institute of the Max Planck Society, Berlin, Germany*
[2]*Instituto de Tecnología Química, Universitat Politècnica de València-CSIC, Valencia, Spain*
[*]*trunschke@fhi-berlin.mpg.de*
[*]*pasuabur@itq.upv.es*

Introduction. Syngas will play an important role during the energy transition to renewables, especially the transformation of CO/CO_2 + H_2 mixtures obtained either from biogas or CO_2 (RWGS). Here, rhodium catalysts are versatile benchmarks. In this work we present a strategy towards the preparation of Rh-containing solid catalysts, which consists in the low-temperature exsolution of Rh species from $ZnFe_{2-x}Rh_xO_4$ mixed oxides with a spinel structure. In a first step, hydroformylation of alkenes was used as a test reaction [1], which is also industrially relevant, but still carried out using Rh-phosphine/phosphite complexes in homogeneous phase [2]. In the recent years the effort has been focused on Rh-containing solids that can emulate the catalytic properties of their homogeneous counterparts [3].

Experimental/methodology. A series of nanosized $ZnFe_{2-x}Rh_xO_4$ (x=0-0.2) mixed metal oxides has been prepared by hydrothermal synthesis. Catalytic tests were carried out in stainless-steel batch reactors with a total volume of 12 mL and magnetic stirring (m_{cat}: 30 mg, 1.5 mL toluene, 1.5 mmol 1-hexene, 40 bar, $CO:H_2$ 1:1). The materials were activated in the reactor prior to the catalytic tests.

Results and discussion. The isomorphic substitution of Rh^{3+} species for Fe^{3+} in the octahedral positions of the $ZnFe_2O_4$ spinel has been successfully achieved by applying a hydrothermal synthesis protocol based on the decomposition of oxalates. Results derived from TPR-H_2, *in situ* Raman spectroscopy and *in situ* XRD experiments during activation of $ZnFe_{2-x}Rh_xO_4$ under reducing conditions indicate that activation temperature and time can be tuned to exsolve Rh species in the form of particles smaller than 1 nm, which remain anchored to a spinel-type metal oxide (Figure 1A). Interestingly, this exsolution process takes place at very low temperatures, in the 150-275 °C range. The reduced metal oxides have been tested in the hydroformylation of 1-hexene (Figure 1B). The materials present catalytic properties comparable to the Wilkinson $RhCl(PPh_3)_3$ homogeneous catalyst, especially at low temperatures, where undesired alkene isomerization can be minimized. No Rh leaching is detected, and the catalysts retain their catalytic properties up to 4 uses. The electronic properties of the metal particles were analyzed by DRIFT spectroscopy of adsorbed CO indicating that the spinel forms an unique functional interface.

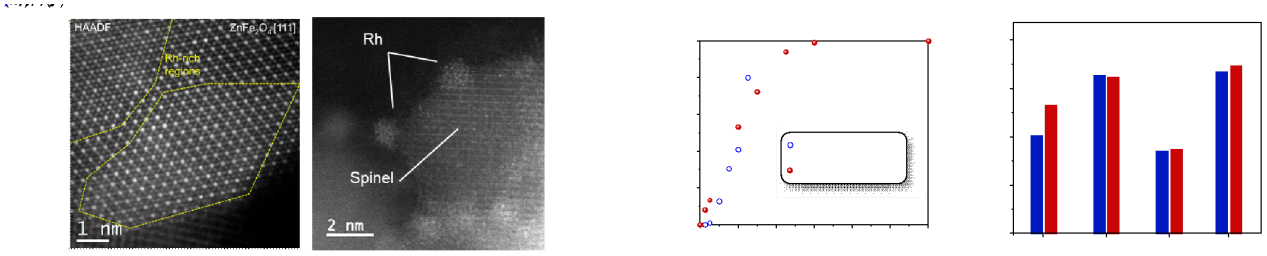

Figure 1. A) High-Resolution HAADF-STEM images of $ZnFe_{1.8}Rh_{0.2}O_4$ activated in 5% H_2 at 275 °C for 1h. B) Catalytic properties in the hydroformylation of 1-hexene for $RhCl(PPh_3)_3$ and activated $ZnFe_{1.975}Rh_{0.025}O_4$ (Rh:1-hexene ratio of 1:500, T=60 °C, 40 bar, $CO:H_2$ 1:1).

Acknowledgments
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How can we profit from merging catalysis with photocatalysis?

Wojciech Macyk,* Taymaz Tabari, Joanna Kuncewicz, Marcin Kobielusz, Zbigniew Sojka

Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland
**macyk@chemia.uj.edu.pl, www.photocatalysis.eu*

Keywords: catalysis, photocatalysis, radical reactions, reactive oxygen species

A fundamental difference between photocatalytic oxidation of pollutants and photocatalytic production of solar fuels should be perceived. Similarly to combustion, oxidation of pollutants is an exergonic process, while water splitting or carbon dioxide reduction are endergonic reactions. In energy downhill processes absorbed light is utilized to overcome the activation energy of elemental steps, *e.g.*, activation of oxygen or C-H bond. The role of photons is therefore to "ignite" the energy downhill reaction. Production of hydrogen from water, or methanol from CO_2, are, however, highly endergonic reactions. Photocatalytic production of solar fuels is a process of solar quantum energy conversion to the energy of chemical bonds. In such processes photons can be considered as reagents. This differentiation is crucial to understand a theoretical limit of quantum efficiencies available in these types of processes. In the energy uphill reactions the energy gain (the energy of chemical bonds) originates from the energy of photons. One absorbed photon can generate one e^-/h^+ pair which can be used in single elemental reduction/oxidation reactions. Therefore, the limit of the overall quantum efficiency, defined as the number of e^-/h^+ redox steps divided by the number of absorbed photons, amounts 1. In the energy downhill reaction the energy evolved in the process can be dissipated as heat (and lost) or can be used to accelerate next elemental, catalytic steps. Taking this into account one can expect the overall quantum efficiency might exceed the unity. In order to facilitate it appropriate catalytic and redox conditions should be provided. A possibility of such reactions, including the design of appropriate catalytic/photocatalytic materials (Figure) will be illustrated and discussed.

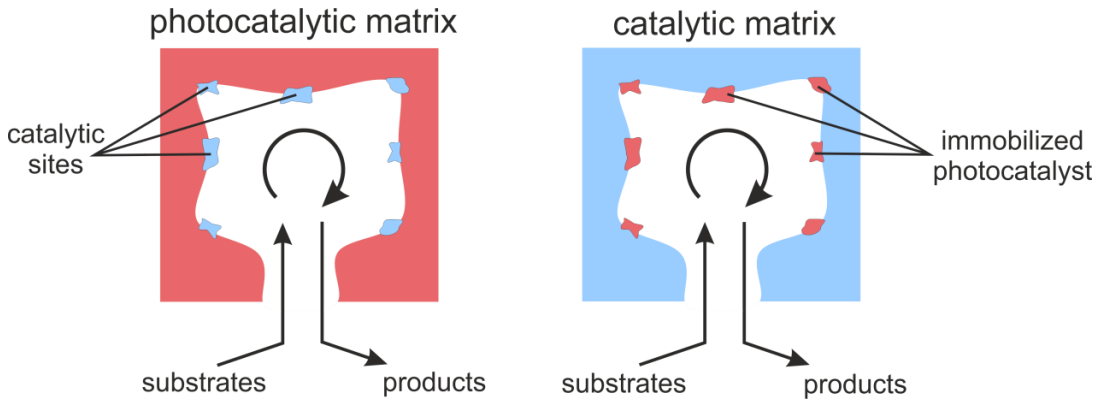

Figure. Two concepts of merging catalytic with photocatalytic materials.

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Bottom-up synthesis of stable platinum dimers on cerium oxide for hydrogen release

Martijn J. Mekkering, Petrus C. M. Laan, Gadi Rothenberg* and Ning Yan*

Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands
g.rothenberg@uva.nl, ning.yan.uva@outlook.com

Keywords: double-atom catalysis, ammonia borane, hydrogen storage

Introduction. Single-atom catalysis (SAC) has the advantage of 100% metal utilization and therefore the highest performance per price unit[1]. Besides an optimization in the surface-to-volume-ratio, another optimization is possible by changing the active site. Some chemical reactions are chemically hindered due to lack of potential binding sites. Double-atom catalysis (DAC) has therefore been a long-standing dream for bridging homogeneous and heterogeneous catalysis. Demonstrating the utilization of DAC is best performed in reactions where two reagents are activated. Ammonia borane hydrolysis is such a reaction which allows the activation of ammonia borane and water[2].

Experimental/methodology. The SACs and DACs were synthesized with following a wetness impregnation technique. $H_2PtCl_6{\cdot}6H_2O$ was used for the SAC and Di-μ-iodobis(ethylenediamine)diplatinum(II) nitrate (PIP) was used for synthesizing the DAC. They were supported on CeO_2 cubes, which were synthesized hydrothermally. The catalytic experiments were performed in a home-built set-up which is efficient in analyzing gas-ouput streams. Ammonia borane was dissolved in water and water was used both as substrate and as a solvent.

Results and discussion. Here we show the thermoconversion of ammoniaborane hydrolysis. The DAC showed a significant improvement in activity compared to the SAC. CO-DRIFTS measurements confirmed a quantitativly similar amount of platinum on the surface. Moreover, XPS measurements showed that the oxidation state of the platinum atoms was the same. This implies that other effects contribute as well to the higher turnover number. Surprisingly, the mechanism of the reaction is the same according to the Arrhenius plot. No discrepancies in the metal-support interactions for the SACs and DACs are possible as the surface structure of each CeO_2 particle is the same.

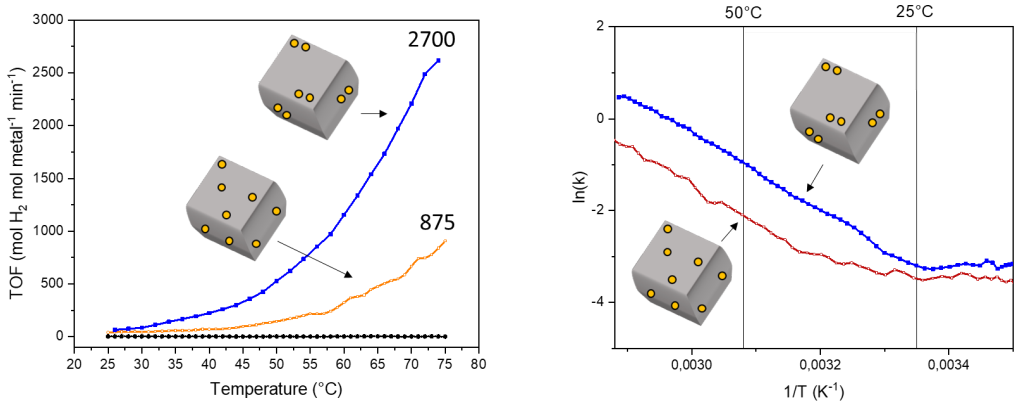

Figure 1 – ammonia borane hydrolysis over SACs and DACs. An increased performance was observed for DACs, while the mechanism was the same.

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Mn-promoted MoS_2 as a catalyst for CO_2 hydrogenation to methanol: Investigating the interaction between MoS_2 and Mn oxides

G. A. S. Alves*, G. Pacholik, T. Wagner, S. Pollitt, M. Latschka, R. Rameshan, C. Rameshan, K. Föttinger [1]

[1]*Institute of Materials Chemistry, Technische Universität Wien, Vienna, Austria*
**gustavo.alves@tuwien.ac.at*

Introduction. With the ongoing scenario of anthropogenic climate change, the capture and utilization of CO_2 has been increasingly considered as an alternative starting point for the production of a variety of value-added products, such as alcohols and hydrocarbons. In this context, the direct hydrogenation of CO_2 into methanol has been most effectively performed using $Cu/ZnO/Al_2O_3$ catalysts, but the applicability of this material at industrial scales is still limited by its low selectivity to methanol, instability of the active phase and surface poisoning in the presence of sulfur-containing gasses. [1]
Because of these constraints, non-metallic catalysts such as MoS_2 might offer a promising alternative due to their high stability and tolerance to sulfur. Pure MoS_2 is typically selective towards CO_2 hydrogenation to methane, although some promoters have been shown to induce CO production instead. [2] In this work, we demonstrate that Mn-promoted MoS_2 can work as a selective catalyst for methanol production from CO_2 hydrogenation as a result of the interaction between MoS_2 and Mn oxides.

Experimental/methodology. Mn-promoted MoS_2 was produced by a hydrothermal method. Ammonium heptamolybdate, thiourea and manganese sulfate were heated in an autoclave with water at 200 °C overnight. The precipitated sulfides were filtered and repeatedly washed with water and ethanol. The powder was dried in vacuum at room temperature, followed by calcination at 400 °C under inert gas.
Material characterization was carried out via X-ray diffraction (XRD), in-situ Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS), Extended X-ray absorption fine structure (EXAFS) and Scanning Electron Microscopy (SEM). Catalytic testing took place with 1g of catalyst in a fixed bed reactor at 21 bar under flow of 1 mL/min CO_2, 3 mL/min H_2 and 1 mL/min He. Prior to each reaction, catalysts were activated at 400 °C under pure H_2. Reaction products were evaluated by gas chromatography.

Results and discussion. Mn-promoted MoS_2 produced via hydrothermal method was shown to present favorable properties as a catalyst for CO_2 hydrogenation to methanol. Although MoS_2 is typically selective towards methane in the presence of H_2 and CO_2 above 180 °C, the addition of Mn precursors to the hydrothermal synthesis of MoS_2 switches catalyst selectivity towards methanol. Interestingly, the highest methanol yield is achieved at temperatures below 200 °C. This enhanced activity under mild conditions may offer promising possibilities for industrial application, given the economical advantage of utilizing lower temperatures.
Material characterization by XRD, EXAFS and in-situ XPS shows that the manganese promoter is initially present as $MnCO_3$, which is converted to bulk MnO with a combination of surface Mn(II) and Mn(III) species after H_2 pretreatment. This composition is maintained at low temperature reaction conditions (< 200 °C), as higher reaction temperatures promote the carbonation of MnO into $MnCO_3$, compromising catalytic activity. Therefore, the results indicate that the synergy between MoS_2 and manganese oxides may be a key factor for the high methanol selectivity during CO_2 hydrogenation.

Acknowledgments
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Resolving the enhanced performance of Mn modified spinel based CO_2 methanation catalysts by combining *ex situ* and *operando* analysis

T. Franken[1*], D. Weber[1]

[1] *Friedrich-Alexander-Universität Erlangen-Nürnberg, Institute of Chemical Reaction Engineering, Group of Catalytic and Electrocatalytic Systems and Processes, 91058 Erlangen, Germany*

[*] *tanja.franken@fau.de*

Keywords: Spinel catalysts, *operando* Analysis, CO_2 methanation, H_2-spillover, selectivity enhancement

Introduction. CO_2 methanation with renewable H_2 from water splitting is a future relevant technology to limit CO_2 emission, close C-circles and enable chemical energy storage. Herein gaining high CH_4 selectivity is essential. Due to oxidation and deactivation Ni based catalysts tend to produce CO as an undesired by-product. This effect is even more pronounced if Co is used as the active sites. Within our contribution we resolve how Mn modified spinel based catalysts yield a superior performance over conventional supported Ni/Al_2O_3 catalysts and what properties lead to their strong improvement in CH_4 selectivity.

Experimental/methodology. Catalysts have been prepared by coprecipitation of the corresponding metal nitrates at a constant pH of 9 and were subsequently filtered, washed and calcined at 800 °C. The catalytic performance was investigated in fixbed flow reactors. Furthermore, catalysts were characterized by XRD, TPR, CO_2-TPD, H_2 & CO chemisorption, CO_2 DRIFTS and *operando* DRIFTS analysis.

Results and discussion. Dependent on the degree of Mn modification in both $NiMn_xAl_{2-x}O_4$[1] and $CoMn_xAl_{2x}O_4$[2] spinel systems a strong increase in activity and CH_4 selectivity was observed at intermediate Mn modification levels of x = 0.375 and x = 0.5, respectively. Both systems show good long term stability. The effect of enhanced CH_4 selectivity is much more pronounced for the Co-based system. By combing several *ex situ*, *in situ* and *operando* analytics we resolved the effect for the Co based spinel. *Operando* DRIFTS analysis suggests, that the reaction mechanism changes from a purely CO intermediate mechanism on Co based catalysts, towards a formate intermediate mechanism on the Mn modified catalysts. The change of reaction mechanism is the main reason for the strongly improved CH_4 selectivity. Obviously, due to Mn modification spillover of H from the metallic sites onto the surface of the full supporting spinel surface gets possible. Together with the stronger basic sites in the Mn modified spinels and the fine distribution of Co sites within the spinel CO_2 gets activated on the full surface of the supporting spinel. Therefore the catalytically active surface is enhanced from the metallic sites only towards the fully available specific surface area of the preactivated spinels. To conclude our contribution presents a novel approach to design catalysts based on mixed metal oxides, that can be tuned for high selectivity and activity thanks to cooperative effects and the high dispersion of elements within common crystalline structures.

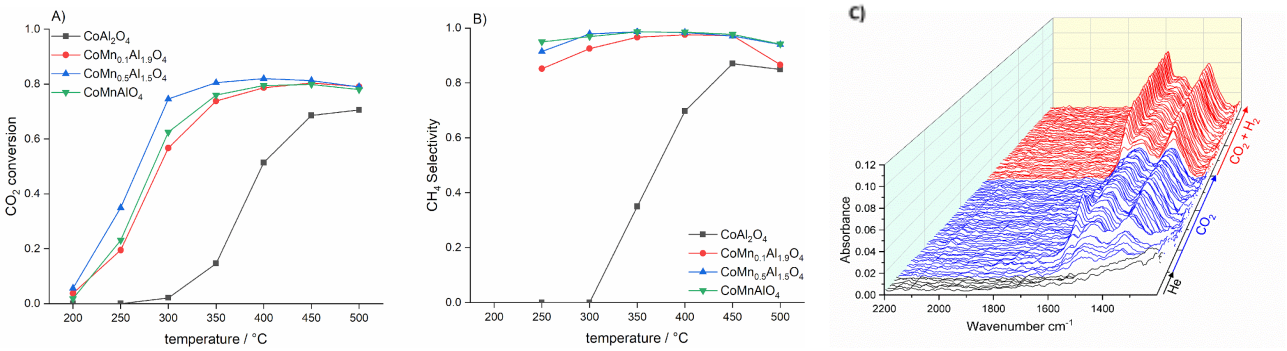

Figure 1: A) Conversion and B) Selectivity of activated Mn modified CoAl-Spinels in the methanation of CO_2 C) Time resolved *operando* DRIFTS spectra under CO_2 Methanation conditions.

Acknowledgments

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High-Efficiency acid-base synergy ZrO_xH_y Catalyst for Amine Regeneration in Post-Combustion CO_2 Capture Process

Cheng Zhou[1], Yuhe Liao[2] , Bert F Sels*[1]
1.Center for Sustainable Catalysis and Engineering, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium.
E-mail: bert.sels@kuleuven.be
2.Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, 510640 Guangzhou, P. R. China

Keywords: CO_2 Capture, Amine, Catalysis, ZrO_xH_y, Acid-base catalysis

Abstract:

CO_2 post-combustion with amine solution is one of the most "ready-to-use" CO_2 capture technics for the transition period from a traditional fossil-based society to a carbon-neutral society. However, the high energy cost of the primary amine regeneration process is one of the pain points for the application. Many catalysts have been developed to solve this problem. However, they are not efficient enough for real applications and are mostly tested in a batch reactor, which is very different from the continuous stripper used in the industry. Herein, we report a highly efficient ZrO_xH_y catalyst, for CO_2 desorption from amine solution. Through the kinetic study results, ZrO_xH_y shows a 2.5 times improvement on the CO_2 desorption rate constant (k_{CAT}) compared with blank in 30 wt% MEA solution in the batch reactor, with good recyclability. This great catalytic improvement is not especially for MEA solution but is also observed in other amines, like 2-Amino-2-methyl-1-propanol (AMP). By combining the kinetic study results and spectroscopic techniques, we found a volcano relationship between k_{CAT} and the terminal /bridge hydroxyl group ratio, where k_{CAT} reached the top at a terminal/ bridge hydroxyl group ratio close to 1. Based on that observation, an acid-base synergy mechanism is proposed in Figure 1. The mechanism is further proved through the operando ATR-FT-IR. To bring this work one step closer to the industrial condition, ZrO_xH_y is also tested with a self-built fix-bed continuous reactor. By using ZrO_xH_y, a 3.5-fold CO_2 desorption rate is achieved under a much shorter (~1/4) contact time compared with blank, showing a more promising prospect for industrial applications.

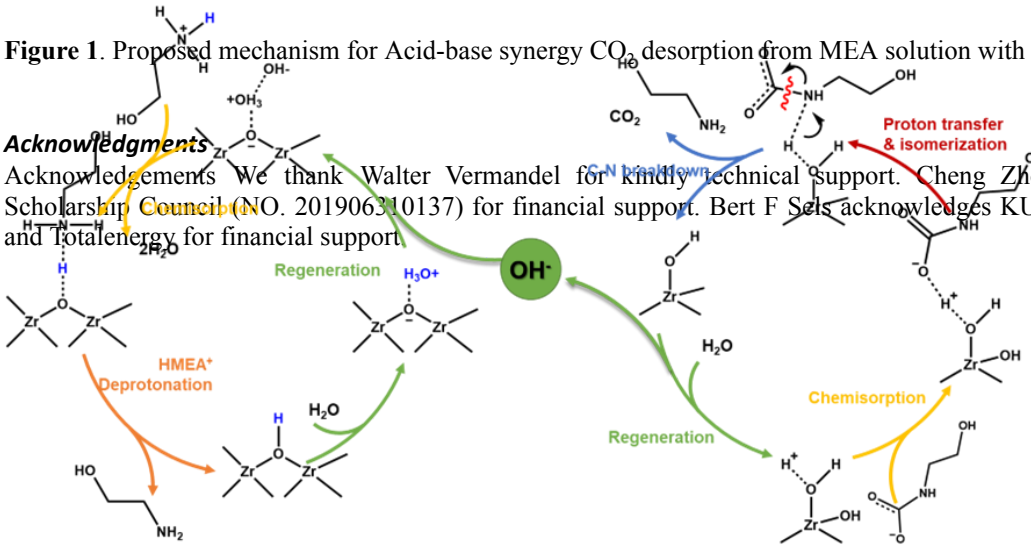

Figure 1. Proposed mechanism for Acid-base synergy CO_2 desorption from MEA solution with ZrOxHy.

Acknowledgments
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Exsolving Fe-X (X= Cu, Co) Catalysts for CO_2 to Synthetic Fuels

S.Saini[1], Q. Cai[1], K. Kousi[1]

[1]*School of Chemistry and Chemical Engineering, University of Surrey, Guildford, UK*
[*]*k.kousi@surrey.ac.uk*

Keywords: Catalysis, exsolution, CO_2 utilisation, light olefins

Introduction: Conversion of CO_2 into valuable chemicals and fuels provides a good solution to mitigate the ever-growing worldwide CO_2 emissions. Various approaches have been considered for CO_2 conversion, among which the thermocatalytic conversion of CO_2 by hydrogenation seems to be very promising due to the diversity of the products that can be produced.[1] However, challenges for this process include the design and preparation of catalysts that can promote activity and product selectivity without compromising stability. It is known that copper (Cu), cobalt (Co) and iron (Fe) are being used in industry to produce fuels and chemicals by CO_2 hydrogenation but easily get deactivated by agglomeration or poisoning.[2] Recent studies demonstrated that catalytically active transition metals substituted on B site of A-site deficient perovskite oxides ($A_{1-x}BO_3$) can emerge on the surface of the perovskite under reducing conditions in the form of metallic nanoparticles. This method is called exsolution and the particles produced are resilient to coking and agglomeration while having increased activity.[3] In this work, six perovskites with exsolved Fe-X (X= Cu, Co) metallic nanoparticles were explored for the CO_2 hydrogenation and show remarkable activity and stability as compared to their traditionally prepared analogues.

Experimental: A modified solid state synthesis method was used to synthesize two families of materials with high ($La_{0.5}Sr_{0.3}Ti_{0.7}Fe_{0.3}O_{3-\delta}$, $La_{0.6}Sr_{0.2}Ti_{0.7}Fe_{0.2}Co_{0.1}O_{3-\delta}$, $La_{0.6}Sr_{0.2}Ti_{0.7}Fe_{0.2}Cu_{0.1}O_{3-\delta}$) and low doping ($La_{0.43}Sr_{0.37}Ti_{0.94}Fe_{0.06}O_{3-\delta}$, $La_{0.43}Sr_{0.37}Ti_{0.94}Fe_{0.04}Co_{0.02}O_{3-\delta}$, $La_{0.43}Sr_{0.37}Ti_{0.94}Fe_{0.04}Cu_{0.02}O_{3-\delta}$), to investigate the effect of doping amount on the extent of exsolution and the amount of active sites on the surface.[4] To exsolve particles, reduction of the synthesized materials was carried out in a controlled atmosphere furnace, under continuous flow of pure H_2 at a range of temperatures (700- 900°C) for 10h. The crystal structure and the purity of the exsolved samples were studied using powder X-ray diffraction (XRD). The morphology of the materials was obtained using scanning electron microscope (SEM, APREO 2). CO_2 hydrogenation was conducted in a continuous fixed bed quartz reactor using 0.25g of catalyst. The activity test was conducted at Weight Hourly Space Velocity (WHSV) 12 L/g.h with H_2/CO_2 ratio of 3:1 balanced in nitrogen. The reaction temperature varied between 250 ^{o}C and 350 ^{o}C in 10 ^{o}C intervals for 30 min at each temperature. Reactants and products were monitored using gas chromatography (micro-GC equipped with thermal conductivity detector).

Results and discussion. The XRD patterns of the as-prepared materials clearly showed that both low and high doping of monometallic and bimetallic dopants were successfully incorporated into the perovskite structure. The particle size and distribution were analysed via ImageJ from the SEM images obtained at different temperatures. Catalytic results showed that the addition of a second metal (i.e. Co, Cu) has a strong influence in the selectivity of the materials owning to both the different exsolution characteristics and the chemistry of the active sites.

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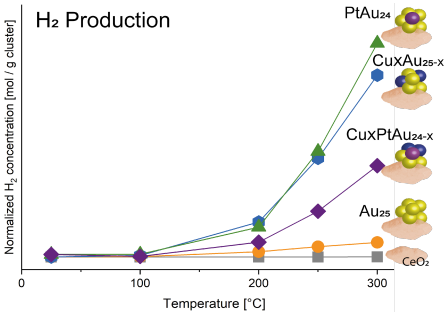
Synergetic effect of Pt,Cu and Au in metal nanoclusters on CeO_2 as atomically precise active sites for WGS reaction: structural dynamics by *operando* XAFS and DRIFTS studies

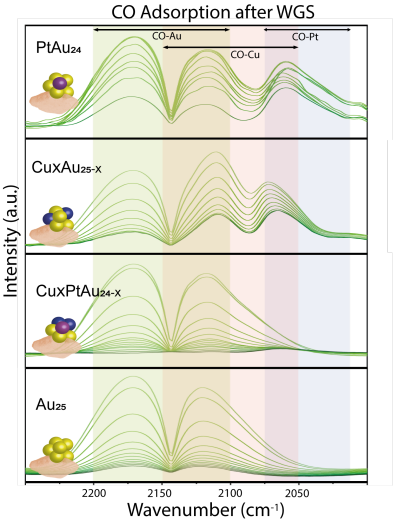
Nicole Müller, Rareș Banu, Adea Loxha, Lorenz Lindenthal, Florian Schrenk, Noelia Barrabés*
[1]*TU Wien, Institute of Materials Chemistry, Getreidemarkt 9/165, 1060 Vienna, Austria*
noelia.rabanal@tuwien.ac.at

Introduction. A major route to obtain clean-energy hydrogen is the catalytic water-gas shift (WGS) reaction. Particle size/structure and metal-oxide interface have been shown to be critical for operation at mild conditions with high activity and selectivity in WGS. Therefore, understanding and controlling catalytic performance at the molecular level is essential for optimal catalyst design. Thiolate protected gold nanoclusters represents a new approach involving novel nanostructures with key atomically controllable parameters. Over the last years, we were able to develop mono- and bimetallic nanoclusters catalysts, tuning their properties with atomic precision and understanding the structure dynamics under reaction conditions by *operando* infrared (IR) and x-ray absorption spectroscopic (XAFS) studies [1-5]. The synergistic effect at the atomic level of Cu, Pt, and Au in terms of activity and selectivity in the WGS reaction was investigated using mono-, bi- and tri-metallic nanoclusters supported on CeO_2 as catalysts.

Experimental/methodology. Atomically precise mono- ($Au_{25}(SR)_{18}$), bi- ($PtAu_{24}(SR)_{18}$; $Cu_xAu_{25-x}(SR)_{18}$) and trimetallic ($Cu_xPtAu_{24-x}(SR)_{18}$) nanoclusters were synthesized, isolated and characterized by UV-Vis and MALDI-MS, based on previous experience [1-5].The trully monodispersed clusters were supported on CeO_2. The cluster catalysts were pretreated by a combined oxidation/reduction process prior to the water gas shift reaction in a continous flow reactor set-up coupled with online with GC and MS analysis. The correlation between the catalytic activity and the structural dynamics under reaction conditions was studied by *operando* DRIFTS and XAFS (Au L_3-edge and Cu K-edge) experiments. Further CO-FTIR experiments were perfomed to complement the surface characterization.



Results and discussion. The kinetic studies with the nanocluster catalysts ($PtAu_{24}$, Cu_xAu_{25-x} and Cu_xPtAu_{24-x}) showed an enhancement of the catalytic activity by shifting the reaction onset to lower temperatures compared to pure Au nanocluster catalysts. Whereas the XAFS analysis at the Au L_3-edge showed the stability of the cluster structure without sintering of the particles during reaction conditions; Cu K-edge together with the IR-CO results revealed the migration of Pt and Cu metal atoms within the cluster. The Pt atom, originally located in the inner core of the cluster, migrated to the surface creating a single atom site, which is stabilized by the Au core cluster structure. In the case of Cu atoms, monodisperse atoms/small clusters form on the Au cluster surface during pretreatment but develop into Pt-Cu and Cu-Au nanoalloy sites in the case of trimetallic nanoclusters during the reaction. Therefore, bimetallic nanoclusters evolved into stable single site in the case of Pt and small cluster with Cu, that increase their catalytic activity in the WGS and show long stability under reaction conditions. However, in the case of the trimetallic clusters, a continuous evolution of the metal species is obseved, which also affects their catalytic performance. Understanding the dynamics of cluster catalysts at the atomic level is important information for the design of optimcal active cluster sites.



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Metal Nanoclusters for Catalysis

Andreas Weilhard,[1] Benjamin Young,[1] Hiba Azim,[1] Luke Norman,[1] Emerson C. Kohlrausch,[1] Israel Cano,[2] Jesum Alves Fernandes[1]

[1]School of Chemistry, University of Nottingham, Nottingham, UK
[2]Faculty of Chemistry, Universidad Complutense de Madrid, Madrid, Spain

Keywords: Nanoclusters, Assembling, Catalysis

Introduction. At the core of our research is a unique method for breaking bulk metals down to single metal atoms (SMA) and then reassembling them to nanoclusters (MNC) size with precise size and chemical composition.[1,2] In this way we can provide a solution for a sustainable use of scarce metals of technological importance (e.g. Pt, Au, Pd), by maximising utilisation of every atom, and to unlock new properties that emerge in metals only at the atomic scale, leading to substituting critical metals with abundant ones, and providing a platform for next generation of materials for catalysis.

Results and discussion. In this work, we will show how we disassemble bulk materials into single atoms and then to keep them as single atoms or reassemble them to nanocluster size in liquid media and powder surfaces and their catalytic applications. Using ionic liquid media as 'support', we have created Pd nanoclusters that combine the features of both heterogeneous and homogeneous catalysts. We determine the atomic structures and electronic environments of a series of metal nanoclusters in ionic liquids at different stages of formation, leading to a discovery of Pd nanoclusters with a core of ca. 1.8 nm surrounded by a diffuse dynamic shell of atoms in $[C_4C_1Im][NTf_2]$. Comparison of the catalytic activity of Pd nanoclusters in alkene cyclopropanation reveals that the atomically dynamic surface is critically important, increasing the activity by a factor of ca. 2 when compared to compact nanoclusters of similar size. Additionally, kinetic studies of cyclopropanation of alkenes mediated by the dynamic Pd nanoclusters revealed an observed catalyst order of 1, underpinning the pseudo-homogeneous character of the dynamic Pd nanoclusters. Using a solid powder, we have atomically dispersed and stabilized Pt atoms on *g*-C_3N_4 using a scalable, ligand-free, whithout allow them to assembly to MNCs. The deposition of Pt on *g*-C_3N_4 improved hydrogen production *ca.* 370 times (5 h reaction) when compared to bare *g*-C_3N_4, thus demonstrating a high activity compared to other reported systems. We ascribe its high photocatalytic activity to the highly dispersed naked Pt species on *g*-C_3N_4, and due to electron-hole pair recombination decrease, thus enhancing the hydrogen evolution.

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A winning combination of CuFe oxide clusters and γ-alumina support for low temperature total catalytic oxidation of volatile organic compounds

T. Žumbar[1], P. Djinović[1], I. Arčon[2], A- Pintar[1], M. Popova,[3] N. Zabukovec Logar,[1,2]
N. Novak Tušar[1,2*]

[1]*National Institute of Chemistry, Ljubljana, Slovenia*
[2]*University of Nova Gorica, Nova Gorica, Slovenia*
[3]*Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences Institution, Sofia, Bulgaria*
[*]*Corresponding Author's E-mail address natasa.novak.tusar@ki.si*

Keywords: Iron-oxide clusters, Copper-oxide clusters, Alumina support, Synergistic effect, Low temperature, Total catalytic oxidation, Toluene

Introduction. Catalytic oxidation is one of the most important processes for removing of low concentration volatile organic compounds (VOCs) from industrial waste gases. [1] Transition metal nanoparticles immobilized on a suitable support are low-cost alternative to currently used noble metal-containing catalysts. [2,3] A synergistic effect was observed in some cases over bimetallic transition metal supported catalysts that enhanced their total oxidation activity at lower temperature in comparison to monometallic ones. [2,3] To study the mentioned phenomenon, CuFe-functionalized γ-alumina was designed. Namely, alumina is one of the most commonly used industrial catalyst supports because it is easily scalable and cost-effective.

Experimental/methodology. Cu-Fe functionalized alumina supports synthesized from ammonium dawsonite ($NH_4AlCO_3(OH)_2$) precursor with different Fe loadings (from Fe/Al=0.005 to Fe/Al=0.05) and constant Cu loading (8 wt.%) were prepared using a two-step synthesis approach. Structure-property-activity relationship of bimetal CuFe-γ-alumina catalyst for the gas-phase total oxidation of toluene as a model VOC at lower temperature (200–380 °C) was studied. A fundamental understanding of the catalyst and the reaction mechanism is elucidated by advanced microscopic (AR TEM) and spectroscopic characterizations (NMR, XAS) as well as by temperature-programmed surface techniques (H_2-TPR, TPD-O_2 TPD/R-toluene, pulsed toluene oxidation reaction).

Results and discussion. By rational design of bimetal CuFe-γ-alumina catalyst, synthesized from dawsonite alumina precursor, the activity in total oxidation of toluene as a model VOC at lower temperature (200–380 °C) is achieved. It was found out that the nature of the metal-support bonding and the optimal abundance between Cu-O-Al and Fe-O-Al species in the catalysts leads to synergistic catalytic activity promoted by small amounts of iron (Fe/Al=0.005). The change in the metal oxide-cluster alumina interface is related to the nature of the surfaces to which the Cu atoms attach. In the most active catalyst, the CuO_6 octahedra are attached to 4 Al atoms, while in the less active catalyst they are attached to only 3 Al atoms. The oxidation of toluene occurs via the Langmuir-Hinshelwood mechanism. The presented material introduces a new family of low-cost and scalable oxidation catalysts with superior efficiency at lower temperatures. Understanding the structure-property-activity relationship of the designed bimetallic oxide catalysts on alumina support is extremely important not only for the described targeted application for air pollution prevention, but also for other applications in heterogeneous catalysis, green chemistry, advanced manufacturing, and furthermore in electrocatalysis and photocatalysis.

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Highly-porous conjugated polyelectrolytes for water absorption and visible light photocatalysis

Sebastijan Kovačič,* Sarah Jurjevec, Tomaž Kotnik, Gregor Žerjav, Albin Pintar

National Institute of Chemistry, Hajdrihova 19, 1001 Ljubljana, Slovenia E-mail: sebastijan.kovacic@ki.si

Introduction. Powdered semiconducting oxides (e.g. TiO_2 or ZnO) are certainly the most widely used solid photocatalysts in heterogeneous photocatalysis, as these materials are cheap and efficient in converting water pollutants to H_2O and CO_2. However, fast recombination of charge carriers, the form factor (i.e., powders) and the inability to absorb in the visible light range severely limit their practical use. Porous conjugated polyelectrolyte polymers (CPeP) exhibiting attractive properties such as high porosity, extensive π-conjugation with visible light activity, and polyelectrolyte character have recently emerged as an interesting alterantive and have attracted much attention for various applications such as heterogeneous photocatalysis, CO_2 capture or absorption.[1],[2]

Experimental/methodology. In this study, various poly(aryleneethynylene; PAE)-based CPeP were synthesised by Sonogashira-Hagihara polycondensation of 1,3,5-triethynylbenzene and various iodinated benzene derivatives as building blocks, using high internal phase emulsions as templates for porosity.[3] In addition to Sonogashira-Hagihara reaction, emulsion templated poly(arylene-cyano-vinylene) and poly(imine) networks have been synthesized using Knoevenagel [4] or Schiff base [5] condensation reactions. The conjugated foams were characterized in detail by solid-state NMR and FTIR spectroscopy, elemental analysis, diffuse reflectance spectroscopy (DRS), photoluminescence (PL), and cyclic voltammetry (CV). Finally, their photocatalytic performance was evaluated using a fluorescent probe molecule technique.

Results and discussion. The resulting highly porous CPeP exhibited significant semiconducting properties in the visible light region due to their π-extended poly(aryleneethynylene) backbone with donor-acceptor character and optical band gaps in the range of 1.70-2.35 eV. Coumarin and $ABTS^{-+}$ were used as probe molecules to image the oxidation and reduction activity within the π-conjugated system of the PAE-based polyHIPE network. The ability of PAE-based polyHIPE to photo-degrade water pollutants was demonstrated by the degradation of the endocrine disrupting component bisphenol A (BPA) dissolved in water under visible light.

Acknowledgments
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Deciphering the Mechanism of Crystallization of MIL-53 and UiO-66 Metal-Organic Frameworks

Olesya Semivrazhskaya,[1] Daniil Salionov,[2] Adam Clark,[2] Nicola Casati,[2] Maarten Nachtegaal,[2] Marco Ranocchiari,[2] Saša Bjelić,[2] René Verel,[1] Jeroen van Bokhoven[1,2], Vitaly Sushkevich[2,*]

[1] *ETH Zurich, Zurich, Switzerland*
[2] *Paul Scherrer Institute, Villigen, Switzerland*
[*] *vitaly.sushkevich@psi.ch*

Introduction. Metal-organic frameworks (MOFs) have been studied in depth by chemists and material scientists because of their tunable adsorption and (electro) catalytic properties as well as diversity of discovered topologies. However, after more than twenty years of research, understanding of mechanisms of their nucleation and growth is still lacking, hence hindering further progress in reproducible synthesis and modulating the size and shape of the crystals, targeted for scale-up. The present work introduces a detailed molecular-level mechanism of the formation of Al-containing MIL-53 and Zr-containing UiO-66 MOFs, unraveled by combining *in situ* time-resolved mass spectrometry, XAS, MAS NMR spectroscopy, and PXRD. We show for the first time how the MOF topology alters the crystallization mechanism by manipulating chemical reactions responsible for both nucleation and growth.[1,2]

Results and discussion. We show that the formation of MIL-53 starts with deprotonation of terephthalic acid, which is required to coordinate aluminum cations, forming various adducts comprising aluminum, terephthalate, hydroxyl, and nitrate fragments. The released protons induce the decrease of pH and hydrolysis of N,N-dimethylformamide to dimethylamine and formate species. The latter interact with aluminum and incorporate into aluminum-terephthalate adducts. The nucleation process starts after achieving the maximal concentration of deprotonated terephthalate in the mixture. The formate anions incorporate into nuclei with a rate similar to the terephthalate one. The complete consumption of terephthalic acid from the solution terminates nucleation and launches the crystallization phase of MIL-53. During this stage, the agglomeration of nuclei occurs, accompanied by the release of monomeric species to the solution, demonstrating that, in contrast to the general belief, a solid-solid crystallization mechanism is in action. Notably, formate species preserve in MIL-53. At the end of crystallization, the soluble $[(CH_3)_2NH_2]_x(NO_3)_x$ salts are found as the main by-products.[1]

The synthesis of UiO-66 is initiated by the autocatalytic formation of soluble zirconium chloroterephthalates via exchange reaction, with the gradual increase of the number of terephthalate linkers in the zirconium coordination environment. The pre-formation of $[Zr_6(OH)_4O_4]$ nodes was not confirmed. A by-product of the exchange reaction is HCl, which accumulates in the solution, leading to a decrease in pH and the formation of a spectroscopically distinct DMF···HCl adduct. This adduct undergoes hydrolysis, leading to free formate species and dimethylammonium chloride. In turn, after reaching ~20% of terephthalate exchange with zirconium chloride, the hydrolysis leading to the formation of the first nuclei starts. This process implies the rapid solution-mediated formation of the $[Zr_6(OH)_4O_4]$ nodes, with no stable sub-stoichiometric zirconium-oxo clusters being detected. The terephthalate linker becomes a part of the nuclei, while formate species formed by hydrolysis of DMF remain intact in the solution, in contrast to Al-containing MIL-53. The nuclei are structurally identical to the secondary building units of UiO-66; however, they lack long-range order, which they gain during growth. Crystal growth represents the rate-limiting step in UiO-66 crystallization, with nucleation proceeding almost 10 times faster, leading to many small crystals with a narrow size distribution of about 200 nm. The synthesis of the MOF ends with the stabilization of pH, complete consumption of Zr precursors from the solution and absorption of residual water and HCl by the pore system of UiO-66.[2]

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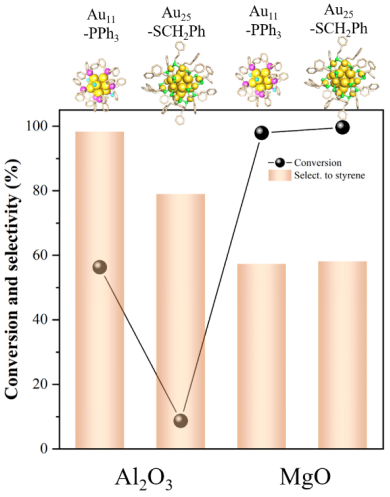
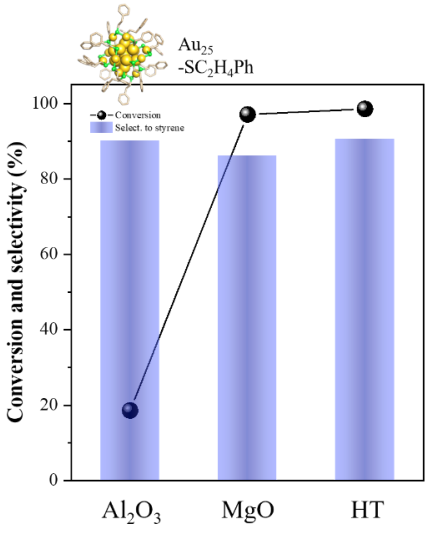
Tuning the Au nanocluster catalyst activity in the selective alkyne semihydrogenation reaction: ligand and support effect

Noelia Barrabés[1,*], Rareș Banu[1], Jesus Mengual,[2] Eduardo Palomares[2], Fernando Rey[2]
[1]*TU Wien, Institute of Materials Chemistry, Vienna, Austria*
[2] *ITQ - Universitat Politècnica de València -(UPV-CSIC), Valencia, Spain*
[*]*noelia.rabanal@tuwien.ac.at*

Introduction. The semihydrogenation of alkynes is of particular interest due to its importance in the production of fine chemicals and polymers. An efficient catalyst that can selectively convert alkynes to alkenes without overhydrogenation to alkanes is needed to remove trace amounts of alkynes before the alkene polymerization process or to convert alkynes to fine chemicals. Recently, gold catalysts is appearing as an alternative related to its lower reductive ability in comparison to Pd, reporting exceptional selectivity and high activity [1]. In order to understand the correlation of the activity and selectivity with structural properties of the catalysts, atomically precise and controlled nanocatalyst is required. Heterogeneous catalytic research of atomically precise gold nanoclusters is an emerging field opening new opportunities for accurate studies of size-dependent properties, atomic structure effects and reaction mechanisms in catalysis. In our previous works, operando XAS and IR measurements have revealed the strong influence of the cluster structure, ligand configuration and support material on their stability and reactivity[2-4]. Therefore, the synergistic effects between the cluster size/structure, the nature of the ligand and the surface area as well as the acid/base properties of the support on the catalytic activity and stability of the supported clusters were investigated in the alkyne semihydrogenation reaction in order to optimize their catalytic performance.



Experimental/methodology. We investigated two different ligand-protected gold nanoclusters (thiolate-protected (SC_2H_4Ph) Au_{25} and phosphine-protected (PPh_3) Au_{11}) in the selective hydrogenation of phenylacetylene to styrene.[5] Alumina with acidic properties, MgO with basic properties, and Mg/Al hydrotalcite (HT), a layered material with an intermediate basicity, were used as support materials. The correlation between the catalytic activity and the structural dynamics and the support properties effect under reaction conditions was studied by DRIFTS, XPS and XAFS studies.



Results and discussion. Strong differences in activity and selectivity were found depending on the cluster-ligand configuration and also on the nature of the support. To determine the influence of the ligand, the catalysts were tested without pretreatment and with pretreament prior to the reaction, where the catalytic activity decreased in the phosphine-protected clusters, while high activity and selectivity was obtained with the thiolate-protected clusters (Fig.1). Preliminary analysis of the spectroscopic studies disclosed the different interaction at the interface between the cluster and the oxide surface depending on the acid-base properties, in agreement with the catalytic behaviour, directing the catalytic performance.

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MAX phase as an efficient heterogeneous catalyst for nitrostyrene chemoselective hydrogenation

Iuliana M. Chirica,[1, 2] Mihaela M. Trandafir,[1] Florentina Neatu,[1] Stefan Neatu,[1] Andrei Kuncser,[1] Varun Natu,[3] Michel W. Barsoum,[3] Mihaela Florea[1],[2*]

[1]*National Institute of Materials Physics, 405A Atomistilor Street, 077125 Magurele, Romania*
[2]*University of Bucharest, Faculty of Physics, 405 Atomistilor Street, 077125 Magurele, Romania*
[3]*Department of Materials Science and Engineering, Drexel University, Philadelphia, USA*
[*]*mihaela.florea@infim.ro*

Introduction. When a molecule contains multiple functional groups, it can be difficult to catalyze the hydrogenation of a single functional group due to the fact that the thermodynamic driving factors are similar. Scientists have developed solid catalysts that selectively interact with one functional group without affecting the others through hydrogenation to solve this issue.[1] MAX phases are well-known for their unusual metal and ceramic properties and numerous investigations on other properties have been undertaken so far. In spite of possessing the necessary qualities for such processes, their potential application as catalysts or as support for catalytic active species had been largely neglected until recently. [2]

Experimental/methodology. Here, we demonstrate how MAX phase can be used to catalyze the chemoselective hydrogenation of a nitro group from functionalized nitroarene, such as 4-nitrostyrene (4-NS) (Figure 1) and 3-nitrostyrene (3-NS). Hydrogenation of these molecules yields functionalized aniline derivatives, which are essential intermediates for a wide variety of chemicals with significant industrial applications [3]. Except for our study, no MAX phase-catalyzed or MAX-supported hydrogenation processes have been reported yet.

Results and discussion. This research indicates that MAX phase materials made of Ti_3SiC_2, Ti_2AlC, or Ti_3AlC_2 may chemoselectively hydrogenate 4-NS to 4-AS (4-aminostyrene) with a complete selectivity (100%), but at a relatively modest conversion rate (less than 4 %). In order to maintain its preferential selectivity and improve the conversion, MAX phase was used as support for various Pd loadings. Based on the data obtained, it is clear that the appropriate Pd content/dispersion onto selective support is crucial, and that exceeding this amount diminishes the MAX phase's selective effect, potentiating only the non-selective effect of Pd [4]. Another essential point in chemoselective hydrogenation reactions is the adsorption and activation of H_2, which takes place differently function of the Pd dispersion. A sample with an extremely low Pd loading (130 ppm Pd, for example) converted 100% of 4-NS with a selectivity of 93% of 4-NS, while increasing the Pd loading resulted in a decrease in selectivity. Furthermore, we improved the turnover frequency by a factor of 100 in comparison to earlier studies in the literature by adjusting the Pd loading (Figure 1). This is achievable by the presence of a large number of metals, most likely as single atoms, which heterolytically activate the H_2 in H^+/H^- pairs, favoring the hydrogenation of polar groups (such as nitro) over non-polar ones [1]. Modified MAX phases were found to be highly efficient and chemoselective, and their development has far-reaching implications for developing low-cost, abundant, environmentally safe metal catalysts.

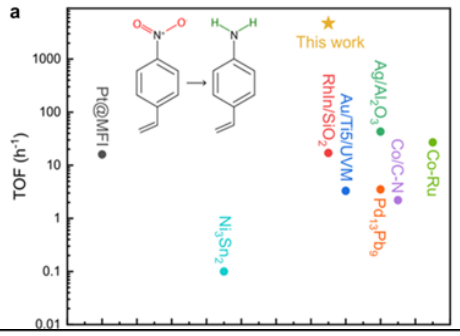

Figure 1: a) TOF results compared with some of the highest reported in the literature for catalysts with 100% conversion and > 80% selectivities of 4-NS to 4-AS.

Acknowledgments

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Ethanol dehydration over hybrid aluminosilicate catalysts prepared by non-hydrolytic sol-gel: One-pot synthesis vs. Surface grafting

Lucie Leonova[1], Zdenek Moravec[1], Petr Sazama[2], Jana Pastvova[2], Damien P. Debecker[3], Ales Styskalik[1*]

[1]*Department of Chemistry, Masaryk University, Brno, Czech Republic*
[2]*J. Heyrovsky Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czech Republic*
[3]*Institute of Condensed Matter and Nanosciences, UCLouvain, Louvain-la-Neuve, Belgium*
[*]*styskalik@chemi.muni.cz*

Keywords: Ethanol dehydration; Aluminosilicate; Non-hydrolytic sol-gel; Hydrophobicity.

Introduction. Hybrid materials based on metallosilicates (including aluminosilicates) exhibit better catalytic performance in various reactions when their surface is more hydrophobic.[1] Generally, the introduction of organic groups can be approached either by onepot synthesis or postsynthetic modification. Herein, a thorough and complex study was performed to evaluate the influence of acidity and hydrophobicity on catalytic performance of aluminosilicate materials in ethanol dehydration.

Experimental/methodology. In this study, the aluminosilicate catalysts were prepared by non-hydrolytic sol-gel (NHSG) either by acetamide elimination or alkylhalide elimination.[2] The non-aqueous condensations provided well-dispersed aluminum atoms (Si/Al = 16) in the porous silica structure. The introduction of organic groups into the structure was approached by two various synthetic strategies – either post-synthetical modification[3] or one-pot synthesis.[4] Structure, porosity, acidity, and hydrophobicity of NHSG-prepared catalysts, and the stability of organic groups were closely followed by MAS NMR studies, N_2 physisorption, IR-pyridine analyses, water adsorption, and TG/DSC, respectively. Finally, aluminosilicates were tested as heterogeneous catalysts in ethanol dehydration to ethylene.

Results and discussion. In the two-step synthesis the fully inorganic matrix was post-synthetically modified by grafting trimethylsilyl groups.[3] The number of reacted ≡Si−OH moieties and thus the trimethylsilyl groups loading was controlled via a temperature vacuum pre-treatment of aluminosilicate samples. While porosity and structure of aluminosilicates after trimethylsilyl groups grafting were very similar to the parent material, the water sorption measurements showed that trimethylsilylated aluminosilicates adsorb 2.5−3 times less water (p/p_0 = 0.3) in comparison to the parent aluminosilicate catalyst. The truly hydrophobic surface of these catalysts did influence the course of ethanol dehydration: The turn-over frequency scaled up with the number of trimethylsilyl groups grafted on the catalyst surface.[3]

In the one-pot synthesis, the methylsilyl groups were introduced and the water sorption measurements revealed that the hydrophilicity of both methylated samples and non-methylated samples were virtually identical.[4] The total number of acid sites did not change upon methylsilyl groups introduction. However, some Brönsted acid sites converted into Lewis acid sites upon methylation. In this case, acidity modulation played a pivotal role in ethanol dehydration. Ethanol conversion increased with the number of acid sites while higher Lewis acid sites content provided an increased selectivity to ethylene.[4]

In conclusion, this study discloses the differences between the one-pot and two-step organic groups introduction into the NHSG-prepared aluminosilicate catalysts. Moreover, it compares the impact of organic groups incorporated by diverse strategies on structure, acidity, and hydrophobicity of aluminosilicate catalysts and put it into the context of ethanol dehydration.

Acknowledgments
The work has been financially supported by the Czech foundation under project GJ20-03636Y and CIISB research infrastructure project LM2015043.

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Rh single-atom sites on oxygen-defective SnO_2 for a selective gas-phase ethylene hydroformylation

Marcos G. Farpón[1], Wilson Henao[1], Philipp N. Plessow[2], Eva Andrés[1], Raúl Arenal[3], Carlo Marini[4], Giovanni Agostini[4], Felix Studt[2] and Gonzalo Prieto[1,*]

[1]*ITQ Instituto de Tecnología Química (UPV-CSIC), Valencia, Spain*

[2]*Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Germany*

[3]*Laboratorio de Microscopias Avanzadas (LMA), INMA (CSIC-UNIZAR), ARAID Foundation, Zaragoza, Spain*

[4]*ALBA Synchrotron Light Source, Barcelona, Spain.*

[*]*Email: prieto@itq.upv.es*

Introduction.

The selective, gas-phase hydroformylation (HF) of light (C_{2-4}) olefins remains an enduring objective for heterogeneous catalysis. The process has been demonstrated with excellent selectivities on molecular Co and Rh catalysts in solution and in supported ionic liquids (SILP).[1] The development of an alternative process in the gas phase, with all-solid catalysts, is attached to various technical incentives and appealing as both an olefin functionalization route as well as a reactive separation alternative to energy intensive cryogenic distillations. Despite intense research efforts, solid catalysts have hitherto shown lower activity and particularly poorer selectivity compared to their molecular counterparts. Herein we report that isolated Rh atoms stabilized on oxygen-defective SnO_2 uniquely unite excellent TOF with essentially full selectivity in the gas-phase hydroformylation of ethylene.[2]

Experimental.

Rh single-atom catalysts (SACs) have been synthesized by oxidative metal dispersion and atom trapping on various MO_2 oxides at a surface-specific metal content of 1.0±0.1 Rh_{at} nm^{-2}. The catalysts have been characterized via XRD, HAADF-STEM and *in situ*/*operando* XAS, CO-FTIR and Raman spectroscopies. Gas-phase ethylene hydroformylation tests were performed in a SS-310 fixed-bed reactor at 20 bar and T= 383-503 K using a feed of $CO:H_2:C_2H_4$ 1:1:1 (v).

Results and discussion.

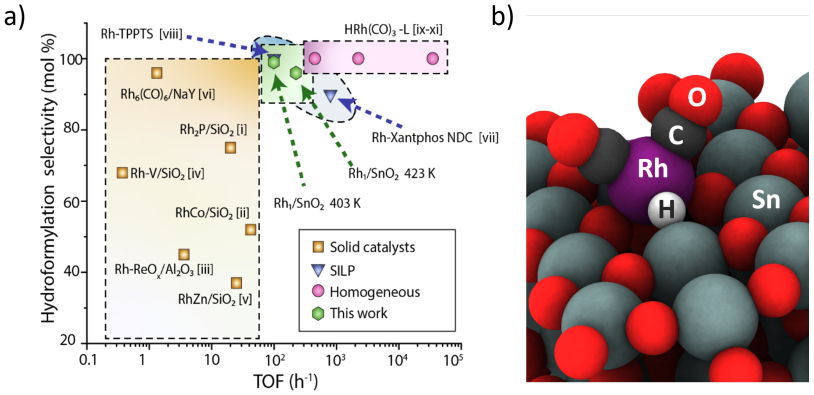

Figure 1: a) Comparison of the performance of a Rh_1/SnO_2 SAC with state-of-art solid and molecular catalysts in solution or on SILP for the gas-phase HF of ethylene. b) Resting Rh hydride dicarbonyl active species predicted by DFT on the surface O-depleted Rh_1/SnO_2(110).

Gas-phase ethylene HF tests revealed modest activities (TOF<4h^{-1}) and HF selectivities (<70% (mol)) for Rh_1 species on ZrO_2 and CeO_2, as well as for Rh_n aggregates on SiO_2, in good accordance with previously reported performances for solid Rh catalysts. In stark contrast, Rh_1/SnO_2 attained TOF values up to 225 h^{-1} alongside hydroformylation selectivities >95 %. This performance is comparable to those thus far exclusive of molecular catalysts operating in liquid media, either in solution or within the ionic liquid overlay on SILP (Figure 1a). *Operando* XAS and *in situ* FTIR and Raman spectroscopies, coupled to periodic DFT calculations, signify the importance of modulating the density of surface bridging-type O_{vac} –the formation of which is energetically facile on SnO_2 under HF conditions – to unlock an unusually high coordination pliability at the mononuclear Rh centers (Figure 1b), responsible for the exceptional ethylene HF performance.

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Ga-Ni Supported Catalytically Active Liquid Metal Solutions (SCALMS) for Selective Alkene Oligomerization

A. Søgaard[1], A. Schmuker[1], A. de Oliveira[2], N. Taccardi[1], M. Haumann[1], P. Wasserscheid[1,2*]

[1]*Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Lehrstuhl für Chemische Reaktionstechnik (CRT), Erlangen, Germany*
[2]*Helmholz-Institut Erlangen-Nürberg (HIERN), Forchungzentrum Jülich, Erlangen, Germany*
[*]*peter.wasserscheid@fau.de*

Keywords: Liquid metal catalysis, alkene oligomerization, single-atom catalysis

Introduction. Supported catalytically active liquid metal solutions (SCALMS) has proved to be a scientific breakthrough in catalytic dehydrogenation of alkanes, which is a key process in chemical energy storage technologies and for applying alkanes as feedstock for chemical transformations [1]. This new class of heterogeneous catalysts consists of catalytically active liquid alloy droplets on a porous support. Ga-rich alloys of Pd, Pt, Rh (Ga > 90 at%) have recently been demonstrated to serve as highly efficient and stable catalysts for dehydrogenation of alkanes and cycloalkanes [1-3]. Previous studies on SCALMS catalysts conclude that the extraordinary and unique catalytic activity arises from the high dynamicity of the surface of the liquid alloys with dynamic appearance and disappearance of single catalytic active metal atoms with a very short residence time at the surface [1,4,5]. In this contribution, we will present our research in the field of selective C-C-linkage reactions as well as the first account of non-precious metal SCALMS – namely the Ga-Ni SCALMS system for alkene oligomerization [6]. As a model reaction, ethylene oligomerization was chosen by the fact that most catalysts for this reaction are molecular in nature and that the oligomerization of lighter alkenes is of great industrial interest.

Experimental section. The silica supported Ga-Ni SCALMS catalysts were prepared by a physical impregnation method using ultrasonication [7]. The catalysts were characterised by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX). Catalytic results have been obtained in a continuous operated fixed-bed reactor setups and analysed by on-line gas chromatography (GC) with a flame ionization detector (FID).

Results and discussion. The SCALMS system of 1.5 at% Ni in Ga on silica ($Ga_{67}Ni/SiO_2$) was found to provide highly stable and efficient catalysis for the oligomerization of ethylene with a high selectivity towards linear C4 compounds, good Ni-based productivity, and long-term stability. The activity of the Ga-Ni SCALMS was found to be highly dependent on the Ga/Ni atomic ratio of the alloy and performance was generally enhanced with increasing Ga/Ni ratio. This behaviour can be linked to the liquid nature of the alloy, where single Ni atoms in the liquid Ga matrix provide reactive single-atom surface sites. The Ga-rich SCALMS systems furthermore outperformed both solid Ga-Ni intermetallic compounds and Ni nanoparticles. Thus, the concept of SCALMS provides a very technical approach for single-atom catalysis and the development of active non-precious metal based SCALMS systems uncovers entirely new frontiers within supported single-atom catalysis.

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Novel synthesis of sub-nanometric high entropy alloy clusters on CeO_2 nanorods

N. Hashimoto[1], K. Mori[1*], N. Kamiuchi[2], H. Yoshida[2], H. Yamashita[1*]

[1]*Graduate School of Engineering, Osaka University, Osaka, Japan*
[2]*SANKEN, Osaka university, Osaka, Japan*
[*]*mori@mat.eng.osaka-u.ac.jp*

Introduction. High entropy alloys (HEAs) are novel metallic materials, consisting five or more elements with near-atomic ratio and form simple single phase like *fcc* or *bcc*. HEAs show unique properties such as extraordinary thermal stability, specific strength and corrosion resistance, such that HEAs are fascinating materials. We previously reported the synthesis of CoNiCuRuPd HEA NPs with a mean diameter of 2 nm, in which there are large gaps between the reduction potentials of the constituent elements, using the pronounced hydrogen spillover effect of TiO_2[1]. In this study, the synthesis of CeO_2 nanorods (CeO_2-NRs) on which sub-nanometer CoNiCuZnPd HEA clusters consisting of 13 atoms were formed with the aid of a pronounced hydrogen spillover effect on readily reducible CeO_2 (110) facets. These clusters also showed a unique structural reversibility in response to repeated exposure to oxidative/reductive conditions, based on the sacrificial oxidation of the non-noble metals.

Experimental/methodology. CoNiCuZnPd/CeO_2-NR catalysts were prepared via a simple impregnation method. In this process, CeO_2-NRs were dispersed in distilled water, after which a metal precursor solution (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}) was added to the suspension. The mixture was subsequently stirred and then evaporated by heating at 60 °C under vacuum. Finally, the specimen was reduced under a flow of hydrogen gas at 600 °C to yield CoNiCuZnPd/CeO_2-NRs.

Results and discussion. The EDX maps of CpNiCuZnPd/CeO_2-NRs acquired over a specific region clearly shows all elements and indicates the formation of highly dispersed quinary CoNiCuZnPd HEA nanoclusters having diameters of less than 1 nm. FT-EXAFS spectra at Pd K-edge demonstrated that the exsistance of not only Pd-Pd bonds but also Pd-M (M=Co, Ni,Cu,Zn) bonds, indicating the formation of quinary HEA particles. In addition, the total coordination number (CN) values (CN_{Pd-Pd}, + CN_{Pd-M})were determined 5.6. The diameter of the quinary CoNiCuZnPd alloy cluster having a CN of 5.6 can be estimated to be 0.79 nm, consisting of 13 atoms, according to the relationship between the CN and the diameter of a Pd cluster.

The catalytic activity were evaluated by the nitric oxide (NO) reduction by hydrogen. The quinary CoNiCuZnPd/CeO_2-NRs exhibited higher activity in comparison with monometallic Pd/CeO_2-NR catalyst(Fig. 1(a)). Futhermore, the stability of HEA catalysts were assessed by using *in situ* XAFS under NO-H_2 conditions. In the case of quinary CoNiCuZnPd/CeO_2-NRs, the randomly distributed Pd atoms formed core nuclei encapsulated by non-noble metal oxide shells (that is, Pd@MO_x; M = Co, Ni, Cu and Zn) via the sacrificial oxidation of the base metals under NO. These structures could be reversibly changed back to well-mixed HEA nanoclusters under a H_2 atmosphere(Fig. 1(b)).

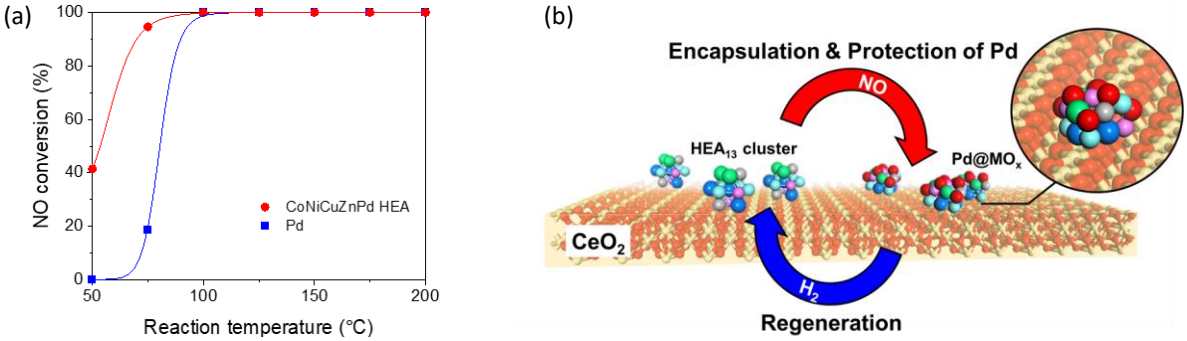

Figure 1 (a) NO reduction activity of CoNiCuZnPd/CeO_2-NRs and Pd/CeO_2-NRs. (b) Proposed structural changes of CoNiCuZnPd/CeO_2-NRs under NO-H_2 conditions.

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Electronic and geometry optimization of Ru nanoparticles exsolution on $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ for ammonia synthesis reaction under mild conditions.

Hayoung Kim[1,2], Deok-Hwang Kwon[1], Ho-Il Ji[1,3], Yongseok Jun[2], Ji-Won Son*[1,2], Sungeun Yang*[1,3]

[1]*Energy Materials Research Center, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea,* [2] *Graduate School of Energy and Environment (KU-KIST Green School), Korea University, Seoul 02841, Republic of Korea,* [3] *Nanomaterials Science and Engineering, Korea University of Science and Technology (UST), KIST Campus, Seoul 02792, Republic of Korea*

** E-mail: syang@kist.re.kr, jwson@kist.re.kr*

Introduction.

Ammonia is attracting wide interest as a next-generation energy carrier in the hydrogen society. In the current ammonia production process (Haber-Bosch process), high temperature is required to overcome the high reaction energy barrier of dissociating stable nitrogen triple bond (N≡N), and high pressure is needed to compensate for the low thermodynamic conversion ratio. The development of a highly active ammonia synthesis catalyst will increase the energy efficiency of ammonia synthesis by lowering the operating temperature and pressure of Haber-Bosch process.[1] The exsolution method has been gaining attention as a method for preparing nanoparticle catalysts with controlled size and distribution and enhanced interaction between the nanoparticle and the support. In this research, exsolved Ru-$BaCe_{0.9}Y_{0.1}O_{3-\delta}$ (BCY) catalyst shows strong metal-support interaction than other samples, which could enhance catalytic activities by accepting electrons from the alkaline earth support and changing the electronic structure of Ru metal. In addition, metal agglomeration was prevented during the catalytic reaction, due to the strong anchoring of Ru nanoparticles on the BCY support. Ammonia synthesis rate of exsolved Ru-BCY catalyst was increased when compared with the Ru-BCY synthesized by the impregnation method, the commonly employed catalyst synthesis method, and the commercial Ru/C catalyst.[2]

Experimental/methodology.

The Ru-doped-BCY support was synthesized using the glycine nitrate process (GNP). The exsolution process was conducted by reducing the resultant powder at a high temperature (1000 °C) under a reducing atmosphere (5% H_2, in Ar-balanced) for 5 h (ex-Ru/BCY). XRD, SEM, TEM, EXAFS, and XPS characterizations revealed that the exsolved Ru nanoparticles have strong metal-support interaction between Ru-BCY. The ammonia synthesis reaction was conducted in a quartz fixed-bed reactor with H_2 and N_2 gas with high purities

Results and discussion.

An exsolution process is implemented to improve catalytic activity by modulating the geometry and electronic structure of Ru. Ru nanoparticles exsolved on a $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ support showed uniform size distribution, 5.03 ± 0.91 nm, and exhibited one of the highest activities, 387.31 $mmol_{NH3}\ g_{Ru}^{-1}\ h^{-1}$ (0.1 MPa and 450 °C). The role of exsolution and $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ support are studied by comparing the catalyst with control samples and in-depth characterizations. The size of the nanoparticle was maintained during the reaction, as the Ru nanoparticles prepared by exsolution were well-anchored to the BCY support with in-plane epitaxy. The electronic structure of Ru is modified by in situ Ba promoter accumulation around the base of the Ru nanoparticles. Therefore, exsolved Ru nanoparticles on BCY (ex-Ru/BCY) showed improved activity for the ammonia synthesis reaction compared to catalysts prepared using the conventional preparation method.

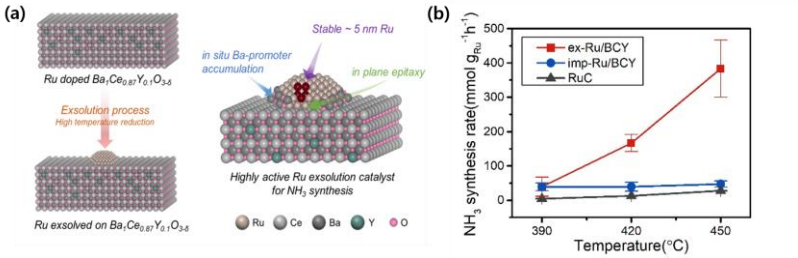

Figure 1 (a) schematic of synthesized exsolved Ru catalyst (b) NH3 synthesis rate of each sample.

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Engineering exsolution catalysts for CO_2 to methanol

S. Soodi[1], L.-P. Merkouri[1], M. S. Duyar[1], K. Kousi[1*]

[1]*School of Chemistry and Chemical Engineering, University of Surrey, Guildford, UK*

[*]*k.kousi@surrey.ac.uk*

Keywords: carbon dioxide hydrogenation, exsolution, methanol synthesis, Ni-Ga catalysts

Introduction. For a sustainable and carbon-neutral future, the atmospheric concentration of CO_2 and energy usage should be limited. Moreover, CO_2 is a cheap carbon source that provides a promising and environmentally friendly pathway to synthesize essential hydrocarbons and chemicals and the catalytic hydrogenation of CO_2 to methanol could be a straightforward solution. Redox exsolution enables us to produce stable and highly active catalysts. In exsolution, homogenously dispersed metallic nanoparticles, emerge at the surface of perovskite support by thermal or electrical reduction. These active sites on the surface of perovskite result in high thermal stability and resistance to poisoning by carbon deposition as well as high catalytic activity. Among transition metals, which are industrially applicable, Ni-Ga-based catalysts have gained increased attention due to their active sites for CO_2 reduction (Fig 1 a).

Experimental/methodology. Ni-Ga exsolution was induced from a $LaCaTiO_3$ support prepared by a modified solid-state synthesis. In order to exsolve particles, the samples were reduced at a temperature in a controlled atmosphere furnace, under a continuous flow of (wet and dry) H_2 at a temperature range of 600-900 °C. The crystalline phase components of all freshly prepared and reduced samples were investigated using powder X-Ray diffraction (XRD): CuKα-radiation, 2θ = 20-90. Rietveld refinement was carried out by the GSAS software. The structure and homogeneity, particle size, population, and local structure/elemental distribution of the exsolved nanoparticles of the materials were analyzed using scanning electron microscopy (SEM) and transition electron microscopy (TEM). The catalytic activity/selectivity was evaluated at atmospheric pressure between 150-300°C.

Results and discussion. Single phase $La_{0.5}Ca_{0.4}Ni_{0.1}Ga_{0.1}Ti_{0.8}O_3$ and $La_{0.48}Ca_{0.41}Ni_{0.1}Ga_{0.06}Ti_{0.84}O_3$ were synthesized. The diffraction patterns of the as-prepared Ni-Ga bimetallic catalysts (Fig 1b), showed characteristic peaks, almost identical to a $LaCaTiO_3$ perovskite implying the successful substitution of both dopants in the perovskite lattice.. The exsolution temperature affected the catalytic performance as different surface ratios between the two dopants were observed. Characterization of catalysts pre and post reaction via SEM-EDX, TEM, etc will also be presented.

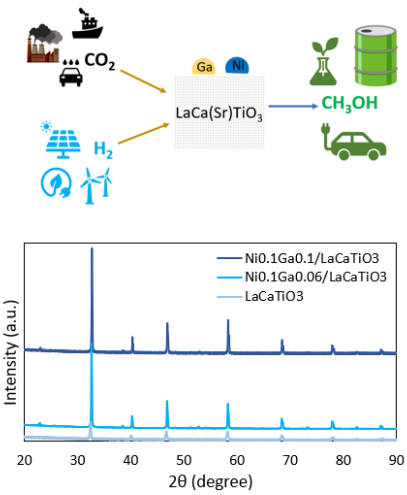

Fig 1: Schematic representation of the concept of the exsolved catalyst for CO_2 hydrogenation to methanol (a), XRD pattern of $LaCaTiO_3$, $Ni_{0.1}Ga_{0.06}/LaCaTiO_3$, $Ni_{0.1}Ga_{0.1}/LaCaTiO_3$ (b).

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Intermittent Ammonia Synthesis over a Cs-promoted Ru/SGCNT catalyst

Shih-Yuan Chen[1]*, Masayasu Nishi[1]*, H. Tateno[1], T. Mochizuki[1], H. Takagi[1] T. Nanba[1]

[1]*National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan.*

Introduction. NH_3 is industrial synthesized by the Fe-catalyzed Haber-Bosch (HB) process under severe conditions (> 400 °C, 10 MPa), which heavily relies on fossil energy, equal to ≈ 2% of the global energy supply and ≈ 1–2% of global CO_2 emissions. Ideally, the Ru-catalyzed HB process for NH_3 synthesis can be performed under milder conditions. However, the Ru-based catalysts, particularly Ru/carbon, generally suffer from H_2 inhibition and deactivation caused by methanation of the carbon framework and sintering of Ru. Super-growth carbon nanotubes (SGCNT) with high stability were developed by Zeon Corporation (ZEON) and AIST using a water-assisted chemical vapor deposition method. Herein, an SGCNT-supported Cs-promoted Ru catalyst with a Ru loading of 10 wt% and a Cs/Ru molar ratio of 2.5 (denoted as Cs-Ru/SGCNT) was prepared for 0.1–8 MPaG NH_3 synthesis under intermittent operation conditions, which simulated electrolysis driven Haber–Bosch (eHB) NH_3 synthesis using photovoltaic electricity. The performance and durability of Cs-Ru/SGCNT catalyst were correlated to the active components of Cs-promoted Ru particles examined by *in situ* studies, and compared with previously reported catalysts [1,2].

Experimental/methodology. The active components of Cs and Ru were impregnated on SGCNT (product code: ZEONANO®SG101, Zeon, Japan), resulting in a Cs-Ru/SGCNT catalyst [1]. NH_3 synthesis was studied in a fixed-bed reaction system equipped with a GC-2014 insutrment (Shimadzu, Japan). The performance and durability of the prepared Cs-Ru/SGCNT catalyst were correlated to the active components (i.e., Cs-promoted Ru nanoparticles), which were studied by *in situ* X-ray absorption spectroscopy (XAS) and temperature-programmed reduction (TPR) under the reaction conditions. The results were compared with the analogs using mesoporous carbon (MPC) and activated carbon (AC) [2].

Results and discussion. Cs-Ru/SGCNT is superior to two analogs of Cs-Ru/MPC and Cs-Ru/AC in catalyzing 0.1-0.9 MPaG NH_3 synthesis, particularly those operated at pressurized conditions (Fig. 1(a)). The *in situ* XAS and TPR studies show that the active components of Cs-Ru/SGCNT are consisted of Ru nanoparticles (2.7 nm) surrounded by well-dispersed Cs species (graph centered in Fig. 1(b)). Figs. 1(b,c) show the long-term NH_3 synthesis of Cs-Ru/SGCNT catalyst under intermittent operation conditions, which simulate eHB NH_3 synthesis process. The results show that Cs-Ru/SGCNT can quickly start up to yield approxiatemly 2.5-3.5% of NH_3 at 250-400 °C (running in the daytime) and stop at 50 °C (shutdown in the night). The performance and durability of Cs-Ru/SGCNT remain nearly unchanged after 7 cycles (~140 h). In summary, the Cs-Ru/SGCNT catalyst with Cs-promoted Ru nanoparticles as the active components are active and durable in NH_3 synthesis under intermittent operation conditions. It would be a potential candidate for eHB NH_3 synthesis with which the electrolytic hydrogen production is varied by the supply of renewable electricity.

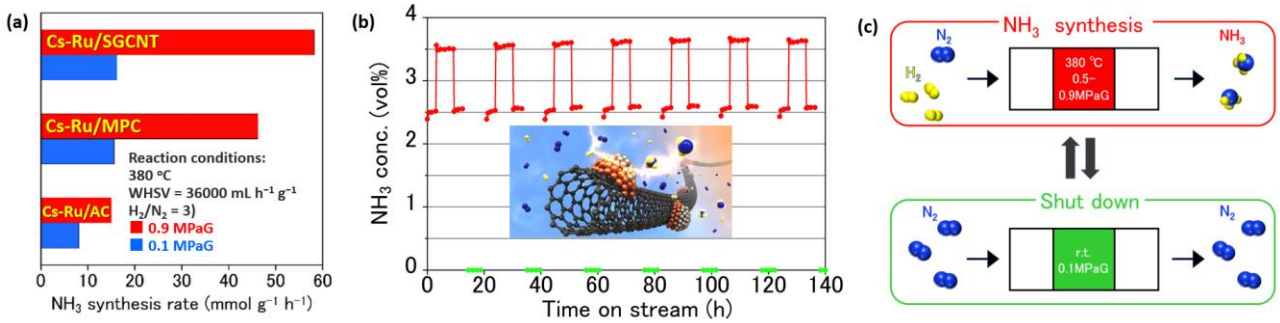

Fig. 1. Intermittent NH_3 synthesis over a Cs-Ru/SGCNT catalyst in comparison with previously reported catalysts.

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Revealing Hydrogen Spillover Pathways in Reducible Metal Oxide Catalysts

K. Shun, K. Mori*, H. Yamashita

Graduate School of Engineering, Osaka University, Osaka 565-0871, Japan
**mori@mat.eng.osaka-u.ac.jp*

Keywords: Hydrogen spillover, Reducible metal oxide

Introduction. Hydrogen spillover is a dynamic phenomenon which is initiated by the dissociation of hydrogen molecules followed by the migration onto the reducible metal oxide supports.[1] Spilled hydrogen atom shows specific behavior compared with gaseous hydrogen, thus it dramatically promotes the reduction of metal ions and the catalytic performance. However, understanding of its dynamic behavior, such as at what temperature it can take place, and what pathway it follows, is still lacking because the observation method is not well established. Our group has reported Ru and Ni, an immiscible metal combination, specifically form RuNi solid solution alloy by an assist of hydrogen spillover on the surface of TiO_2[2]. In this work, we evaluated hydrogen spillover pathways in typical reducible metal oxide such as TiO_2, CeO_2 and WO_3 by combining Ru-Ni alloy nanoparticle formation, *in-situ* techniques, kinetic analysis, and density functional theory calculation.

Experimental/methodology. $RuCl_3{\cdot}3H_2O$ and $NiCl_2{\cdot}6H_2O$ were supported on TiO_2 by conventional impregnation method, after which the sample were reduced under H_2 dosage at a heating rate of 5 ^oC/min up to 300 ^oC to obtain RuNi/TiO_2. Catalysts with CeO_2 and WO_3 as their supports were also prepared by the same method. In order to evaluate the alloy effect of Ru and Ni in the catalytic reaction, the prepared catalyst was applied to the hydrogen production reaction from ammonia borane (AB ; NH_3BH_3).

Results and discussion. RuNi/TiO_2 and RuNi/CeO_2 showed enhanced activity over those of corresponding monometallic Ru catalysts in the hydrogen production reaction from AB indicating the formation of RuNi solid solution alloy nanoparticles. On the other hand, RuNi/WO_3 didn't show any activity improvement compared with that of Ru/WO_3 indicating the segregation of Ru and Ni. These results suggest that hydrogen spillover occurred on the surface of TiO_2 and CeO_2, while hydrogen spillover is absent on the surface of WO_3. Systematic characterization such as *in-situ* XAFS, *in-situ* DRIFT and MS measurements under the H/D exchange reaction were performed in order to evaluate the hydrogen spillover pathways for each support. These results demonstrated that hydrogen spillover on TiO_2 and CeO_2 preferentially proceeded on their surface rather than within their bulk phases. Conversely, hydrogen spillover favorably occurred within the bulk prior to the surface over WO_3. (Figure 1).[3]

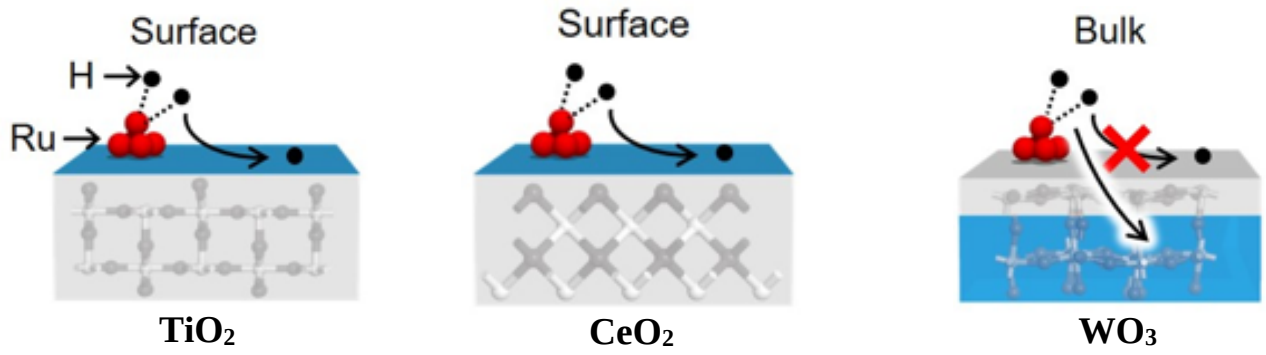

Figure 1. Proposed spillover pathways for TiO_2, CeO_2, and WO_3.

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Metathesis of ethylene with 2-butenes over MoO_x-based catalysts: effect of support on catalyst activity and mechanistic insights into carbene formation

T. Otroshchenko*, Q. Zhang, E.V. Kondratenko

Leibniz-Institut für Katalyse e.V., Albert-Einstein-Str. 29a, 18059 Rostock, Germany

Keywords: metathesis, propene, carbenes, molybdenum oxide

Introduction.

Metathesis of ethylene with 2-butene to propene over catalysts with supported oxides of Mo, Re or W is attractive from both industrial and fundamental viewpoints. From a mechanistic viewpoint, the metathesis reaction occurs with participation of catalytically active metal-carbenes,[1] which must be formed *in situ* upon reaction of feed olefins with supported metal-oxide species. The main purpose of the present study was to investigate the influence of the kind of support on catalyst activity in the metathesis of ethylene with 2-butene as well as to elucidate mechanistic insights of carbene formation through the reaction of highly dispersed MoO_x species with ethylene or 2-butenes. Such knowledge would provide a basis for rational catalyst design and optimization of treatment/reaction conditions.

Experimental/methodology.

A series of Mo-containing catalysts were prepared by incipient wetness impregnation of pre-calcined oxidic suppports (SiO_2, Al_2O_3, ZrO_2, Al_2O_3-SiO_2, ZrO_2-PO_4 or TiO_2-SiO_2) with an aqueous solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$. The solids were dried in air at 110°C overnight and calcined at 500°C for 8 h. The catalysts were characterized by H_2-TPR, NH_3-TPD, C_2H_4-TPD, C_4H_8-TPD, UV-vis and DRIFT spectroscopy. Catalytic tests were performed at 50°C in a fixed-bed reactor with a feed consisting of 45.5 vol% C_2H_4 and 45.5 vol% trans-2-C_4H_8 in N_2.

Results and discussion.

The kind of support strongly influences an apparent Mo-related turnover frequency (TOF_{Mo}) of propene formation (Figure 1). The catalysts based on individual metal oxides showed lower TOF_{Mo} than their counterparts on the basis of promoted/mixed oxides.[2] The TOF_{Mo} values of Mo/ZrO_2-PO_4 and Mo/TiO_2-SiO_2 are more than 350 and 100 times higher than those of Mo/ZrO_2 and Mo/TiO_2, respectively. The higher activity of catalysts based on promoted or mixed-oxide supports is more likely related to the presence of lattice defects created in the support materials after their promotion. Such defects may facilitate the transformation of MoO_x to Mo-carbenes under reaction conditions or improve the intrinsic activity of the latter.

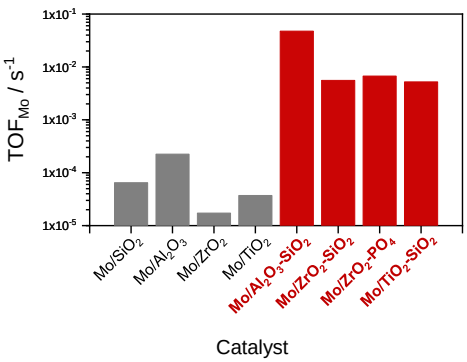

Figure 1 The Mo-related propene formation rate (TOF_{Mo}) at 50°C over different catalysts.

It has also been demonstrated that TOF_{Mo} can be increased by creation of a certain type of hydroxyls in the vicinity of MoO_x through the modification of support surface with non-metallic promoters (S, Cl or P).[3] Such hydroxyls participate in 2-butene adsorption facilitating transformation of MoO_x into active Mo-carbenes. The results of C_2H_4-TPD, C_4H_8-TPD as well as *in situ* DRIFTS experiments led us to the conclusion that 2-butene but not ethylene is able to convert MoO_x species into Mo-carbenes at 50°C. The latter open the possibility for ethylene engagement into the metathesis reaction.

The findings elucidated in the current work open new possibilities for purposeful preparation of supports and catalysts on their basis for low-temperature propene formation from ethylene and 2-butenes and provide insights into the role of individual olefins for *in situ* formation of Mo-carbenes from MoO_x.

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Understanding and Controlling Surface Sites in Silica-supported GaO_x Shells for Isobutane Dehydrogenation

Zixuan Chen[1], Nora Zimmerli[1], Alexander Yakimov[2], Christophe Copéret[2], Pierre Florian[3*], Paula M. Abdala[1*], Alexey Fedorov[1*], Christoph R. Müller[1*]

[1] *Department of Mechanical and Process Engineering, ETH Zürich, 8092 Zürich, Switzerland*
[2] *Department of Chemistry and Applied Biosciences, ETH Zürich, 8093 Zürich, Switzerland*
[3] *CNRS, CEMHTI UPR3079, Univ. Orléans, F-45071 Orléans, France*
pierre.florian@cnrs-orleans.fr; abdalap@ethz.ch; fedoroal@ethz.ch; muelchri@ethz.ch

Keywords: atomic layer deposition, gallium oxide, surface sites, BDH.

Introduction. Materials based on Ga_2O_3 have been widely used as heterogeneous catalysts for alkane dehydrogenation reactions.[1] In this context, supported or unsupported Ga_2O_3, in which surface Ga^{3+} sites reside in different coordination environments, have been studied with the aim to correlate specific surface properties (such as the Lewis acidity strength) with their catalytic performance.[2] Towards this end, understanding the role of different Ga^{3+} sites as well as controlling the coordination geometry and acidity (Lewis and Brønsted) of surface and interfacial sites are necessary for the rational optimization of Ga-based dehydrogenation catalysts. Here, we utilized atomic layer deposition (ALD) to prepare GaO_x/SiO_2 materials with precisely controlled surface sites. The coordination environment of Ga and the surface acidity of the prepared materials were studied by a variety of methods including Ga K-edge XAS, ^{71}Ga MAS NMR and ^{15}N DNP SENS using pyridine as a probe molecule and the results were correlated to the catalytic performance in isobutane dehydrogenation (BDH).

Experimental/methodology. TMG1-, TMG5- and TMG10-$SiO_{2\text{-}500}$ materials were prepared by 1, 5 or 10 ALD cycles of trimethylgallium (TMG, 300 °C deposition temperature) onto silica that had been partially dehydroxylated at 500 °C (SiO_{2-500}); ozone was used as an oxidant.[4] The as-prepared materials were subsequently calcined in synthetic air at 500 °C for 4 h (5 °C min^{-1}) to give Ga1-SiO_{2-500}, Ga5-SiO_{2-500}, Ga10-SiO_{2-500} materials (4.9, 18.2 and 31.9 wt% Ga, respectively, according to elemental analysis).

Results and discussion. Figure 1a presents ^{15}N DNP SENS spectra of Ga1-, Ga5-, Ga10-SiO_{2-500} after the desorption of ^{15}N-pyridine (Py) at 150 °C. Resonances due to mild LAS (250-256 ppm), strong LAS (233-237 ppm) and strong BAS (201 and 216-221 ppm) are observed. The relative intensity of these peaks varies with the thickness of the GaO_x shell such that abundant strong BAS and strong LAS are found mostly in Ga1-SiO_{2-500}. With the growth of the GaO_x layer, the relative fraction of BAS with respect to that of LAS decreases, reaching its lowest ratio in Ga10−SiO_{2-500}. Also, the fraction of medium LAS increases with an increasing thickness of the GaO_x layer. Next, the surface acidity of the prepared GaO_x/SiO_2 materials was correlated with their catalytic performance in BDH (Figure 1b). Ga1-SiO_{2-500}, the catalyst that contains more abundant strong LAS is more active (per Ga) and stable in BDH than Ga5- and Ga10-$SiO_{2\text{-}500}$ (Figure 1b). ^{71}Ga MAS NMR and surface studies allow to associate strong and mild LAS with tetracoordinate and pentacoordinate Ga sites, respectively. Overall, our results indicate that strong LAS drive activity in BDH while mild LAS lead to catalyst deactivation through coking.

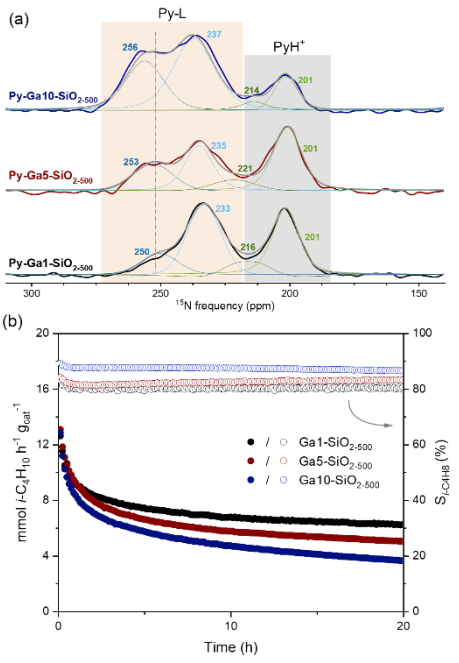

Figure 1. (a) ^{15}N-DNP SENS spectra of Py-Ga1-, Ga5-, Ga10-$SiO_{2\text{-}500}$. (b) Activity and selectivity to isobutene over 20 h time-on-stream (500 °C, WHSV = 8.5 h^{-1}).

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Copper-Decorated Iron Carbide Nanoparticles Heated by Magnetic Induction as Adaptive Multifunctional Catalysts for the Selective Hydrodeoxygenation (HDO) of Aldehydes

S.-H. Lin[1,2], W. Leitner[1,2], A. Bordet[1*]

[1]*Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany*
[2]*Institute of Technical and Macromolecular Chemistry RWTH Aachen University, Aachen, Germany*
[*]*alexis.bordet@cec.mpg.de*

Introduction. The selective HDO of aldehydes to methylene units in the side chain of multifunctional aromatic substrates is an important transformation with applications ranging from the production of fine chemicals to the upgrading of biomass feedstock to value-added chemicals.[1] To provide alternatives to stoichiometric methods that involve toxic reagents and wastes, recent efforts focused on the development of catalytic systems possessing such reactivity. However, the development of catalytic systems fulfilling the requirements of high yields, selectivity, and environmental compatibility remains a challenge.

Experimental/methodology. Magnetic induction offers the possibility to heat directly magnetic catalysts in an extremely localized, rapid, and energy efficient way, saving the need to heat the whole reactor environment. In turn, this may result in milder overall process temperatures and lower energy consumption.[2] In the present work, Cu-decorated iron carbide nanoparticles (Cu@ICNPs) were prepared, characterized, and used as catalysts for the selective HDO of aldehydes using magnetic induction heating. (Fig. 1) The impacts of catalyst structure and composition, as well as of the heating mode (classical vs. magnetic induction) were carefully investigated.[3]

Results and discussion. When heated by magnetic induction, Cu@ICNPs were found highly active and selective for the HDO of aromatic aldehydes to aromatic alkanes under mild conditions (3 bar H_2, 105 °C). As a result, a broad variety of aldehydes could be readily hydrodeoxygenated under these conditions, while no HDO activity was observed even at 200°C. These results indicate that with magnetic induction heating, the reaction proceeds at the surface of the Cu@ICNPs at a temperature much higher that what can be measured at the surface of the reactor, confirming a very localized heating of the catalyst. Interestingly, the catalyst's adaptivity to intermittent power supply was demonstrated by stopping and re-starting the AC magnetic field regularly. (Fig. 1d) This approach is simple and flexible, and can pave the way toward the development of other magnetically-responsive adaptive catalytic systems capable of promoting challenging transformations under mild conditions through magnetic induction heating.

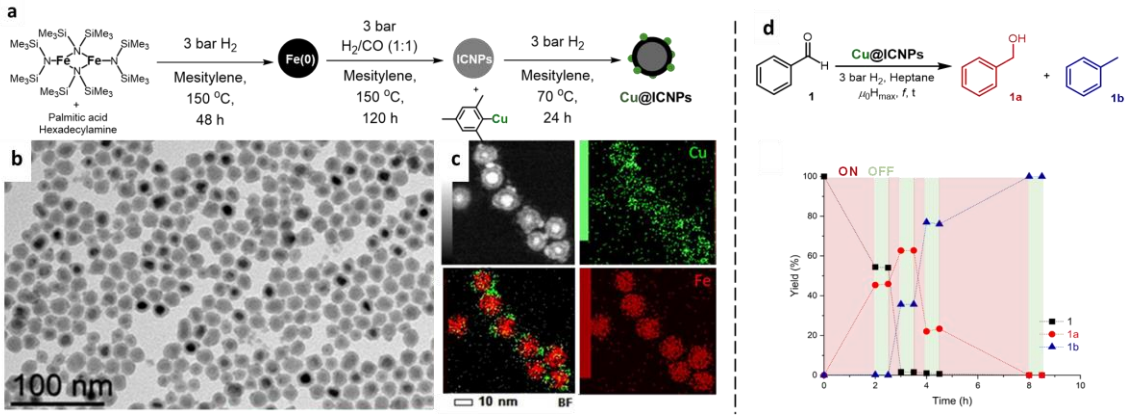

Figure 1. a-c) Synthesis and characterization of Cu@ICNPs. d) Time profile of the HDO of **1** under magnetic induction. Reaction conditions: **1** (35.5 mg, 0.33 mmol, 15 eq.), Cu@ICNPs (10.0 mg, 0.023 mmol Cu), heptane (0.5 mL), H_2 (3 bar), 72 mT, 350 kHz.

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Scalable laboratory synthesis of Cu-based methanol catalysts

S. Pitter[1*], L. Warmuth[1], D. Guse[2], K. Herrera Delgado[1], M. Herfet[1], M. Kind[2], T. Zevaco[1]

[1] *Institute of Catalysis Research and Technology, KIT, Karlsruhe, Germany,* [2] *Institute for Thermal Process Engineering, KIT, Karlsruhe, Germany,* [*] *stephan.pitter@kit.edu*

Keywords: Cu-based catalysts, methanol synthesis, precipitation, catalyst synthesis scaleup

Introduction. Methanol is considered one of the key intermediates on the way to a transformation towards sustainable carbon cycles, due to its physicochemical properties. Methanol also continues to offer the option of a chemical energy store that can be transported over longer distances. Based on conventional technologies, production facilities in many places are already under construction that rely on renewable sources for starting materials (H_2, CO_2) and energy. In addition, various technological options are being examined which, in contrast to conventional, centralized and large-scale production, are aimed at smaller, decentralized production sites.

In the future, more robust technologies will also require further development of the underlying process technology, in which the use of tailored catalysts plays a central role.[1] Important developments of Cu-based catalysts have contributed both to the fundamental understanding of the functioning, hence significantly improving the materials in direction of their industrial application. However, the transferability of findings from academic research into process engineering development remains a challenge, which is increasingly addressed by the use of high-throughput-experimentation (HTE) and, more recently, by the application of Artificial Intelligence (AI) supported material development.[2]

Experimental/methodology. Our approach is to engineer the generation of Cu/Zn-based catalytically active materials to provide robust data for quality control and subsequent scale-up during their lab-scale development. Basis of our approach is the semi-continuous co-precipitation, where initial precipitation takes place in a micromixer under highly turbulent conditions within a very short period of time to achieve largely identical conditions for the subsequent aging of the initially precipitated particles.[3] This procedure offers advantages with respect to the homogeneity of the malachite-based crystal phases formed after aging and can be adjusted via the operating parameters towards optimized macroscopic properties (e.g. morphology, surface).[4]

Results and discussion. In this contribution, we report on a detailed study of the preparation of $Cu/ZnO/ZrO_2$ catalysts that are particularly suitable for the production of methanol from CO_2-rich syngas. We are investigating the complex dependencies of the formation and restructuring of the crystal phases at different metal ratios, pH ranges and temperatures for precipitation and aging. This knowledge can be used to further enhance the catalytic properties after calcination and reduction. An example of such dependence is the difference in productivity (activities) of a series of $Cu/ZnO/ZrO_2$ catalysts in catalytic tesst, which differ only in the fact that precipitation and aging during catalyst precursor synthesis takes place at different temperatures, with an optimum of the catalytic activity at 55 °C. Using a variety of methods to characterize these materials, it is shown which structure-activity relationships play a prominent role in order to further promote catalyst development. Time-dependent formation of the crystal phases during aging will be discussed, which is relevant for further development of catalyst production. In addition, we will demonstrate that catalyst material in the range of several hundred grams can be produced in a short time already on laboratory scale by means of semi-continuous co-precipitation.

Acknowledgment

F. Kreißig, D. Deutsch, M. Zimmermann, G. Niquini, B. Lacerda de Oliveira Campos, for their support in material synthesis and for analytical measurements; Helmholtz-Program MTET and Helmholtz Innovation Pool for funding.

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Scalable laboratory synthesis of Cu-based methanol catalysts

S. Pitter[1*], L. Warmuth[1], D. Guse[2], K. Herrera Delgado[1], M. Herfet[1], M. Kind[2], T. Zevaco[1]

[1] *Institute of Catalysis Research and Technology, KIT, Karlsruhe, Germany,* [2] *Institute for Thermal Process Engineering, KIT, Karlsruhe, Germany,* [*] *stephan.pitter@kit.edu*

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Cyclohexanone oxime production via in-situ generated H_2O_2: a rival to industrial production.

Richard J. Lewis[1]*, Kenji Ueura[2], Xi Liu[3,], Liwei Chen[3], Simon J. Freakley[4], Yasushi Yamamoto[2] and Graham J. Hutchings [1]

[1] *Max Planck–Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK.*
[2] *UBE Industries, 1978-5, Kogushi, Ube, Yamaguchi 755-8633, Japan.*
[3] *School of Chemistry and Chemical, In-situ Centre for Physical Science, Shanghai Jiao Tong University, Shanghai, 200240, P. R. China.*
[4]*Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK.*

[*]*LewisR27@Cardiff.ac.uk*

Keywords: Hydrogen peroxide, In-situ ammoximation, Palladium-gold alloys.

Introduction. Cyclohexanone ammoximation to the corresponding oxime, a precursor to Nylon-6, is one of the best examples of an industrial process that utilises preformed H_2O_2.[1] Decoupling oxime synthesis from industrial H_2O_2 production would lead to significant environmental and financial savings.[2] However, until recently no alternative approach has been reported that is simple or robust enough to replace current technology. Within this submission, we report that despite the challenging reaction conditions, the in-situ synthesis of H_2O_2 from the elements is not only compatible with oxime production but rivals the current industrial process, achieving yields of the oxime in excess of 95%, with these findings reported in recently in a series of leading scientific journals [2-4].

Experimental/methodology. Catalyst synthesis follows a conventional wet impregnation of precious metal salts onto a TS-1 carrier. Evaluation of catalyst activity towards in-situ ketone ammoximation is conducted using a high-pressure batch regime under industrially reaction conditions, utilising dilute streams of H_2 and O_2.

Results and discussion. AuPd nanoalloys in conjunction with TS-1 are shown to be highly active towards the ammoximation of cyclohexanone to the corresponding oxime via in-situ H_2O_2 production, achieving cyclohexanone oxime yields which rival the current industrial process. Through extensive study, the key role of Au in promoting reactivity and stability is identified (Figure A) and our approach is shown to be applicable to a range of ketones (Figure B). The optimal catalyst formulation was observed to be stable up to 200 h on-stream, under industrially relevant reaction conditions. Detailed techno-economic assessment reveals that through the in-situ approach financial savings of approximately 13% can be achieved over the current industrial process.

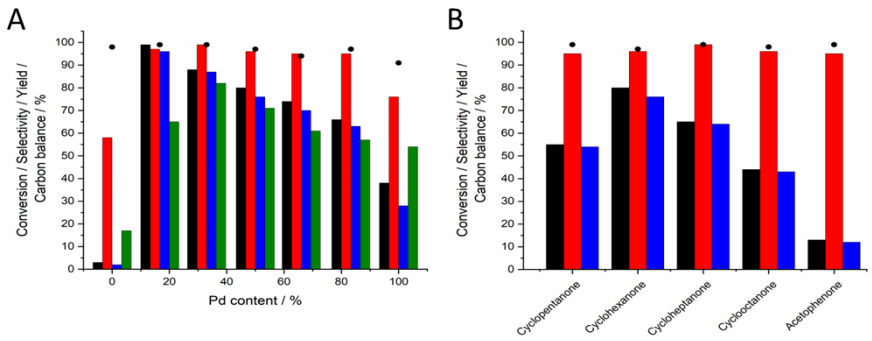

Figure A. The effect of Au:Pd ratio on catalytic activity towards cyclohexanone ammoximation. **Figure B.** Versatility of the in-situ approach to other substrates. **Ammoximation reaction conditions:** Ketone (2 mmol), NH_4HCO_3 (4 mmol), 5% H_2/N_2 (420 psi), 25% O_2/N_2 (160 psi), catalyst (0.075 g), TS-1 (0.075 g), t-BuOH (5.9 g), H_2O (7.5 g), reaction time 3 h, reaction temperature 80 ^{O}C, stirring speed 800 rpm. ***Key*:** Conversion (*black bar*), oxime selectivity (*red bar*), oxime yield (*blue bar*), H_2 selectivity (*green bar*), carbon balance (*black circles*).

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Low-Valent Manganese Atoms Stabilized on Ceria for Nitrous Oxide Synthesis

I. Surin[1*], Z. Tang[1], J. Geiger[2], S. Damir[1], H. Eliasson[3], M. Agrachev[1], F. Krumeich[1], S. Mitchell[1], V. A. Kondratenko[4], E. V. Kondratenko[4], G. Jeschke[1], R. Erni[3], N. López[2], and J. Pérez-Ramírez[1]

[1]*ETH Zürich, Zürich, Switzerland*
[2]*Institute of Chemical Research of Catalonia, Tarragona, Spain*
[3]*Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland*
[4]*Leibniz-Institut für Katalyse, Rostock, Germany*
[*]*isurin@ethz.ch*

Keywords: ammonia oxidation, single-atom catalysis, cerium oxide, manganese, nitrous oxide

Introduction. In the modern endeavour for sustainability and process intensification in the chemical industry, selective oxidations of hydrocarbons constitute a key challenge. In this regard, nitrous oxide, N_2O, a mono-oxygen donor, offers an effective solution, unlocking the path towards more efficient and direct manufacture of an array of bulk chemicals, such as propylene oxide and phenol.[1] However, its high cost, stemming from the conventional production route via ammonium nitrate decomposition, precludes industrial implementation. Accordingly, direct ammonia, NH_3, oxidation to N_2O, a more facile and economical process, offers an attractive alternative but requires the development of a suitable catalyst.

Methodology. The performance of manganese-based catalysts in continous-flow NH_3 oxidation to N_2O is evaluated. The structure of the best system is elucidated by advanced microscopy, electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS) analysis. Advanced mechanistic studies by temporal analysis of products and density functional theory simulations are conducted.

Results and discussion. We report low-valent manganese atoms stabilized on ceria, CeO_2, as the first stable catalyst for NH_3 oxidation to N_2O, exhibiting two-fold higher productivity than the state-of-the-art Au nanoparticles on CeO_2.[2] The single-atom low-valent nature of the catalyst is revealed by means of advanced microscopy, EPR and XPS analyses (**Fig. 1a-c**). The reaction proceeds via a Mars-van Krevelen mechanism, with participation of lattice O species of CeO_2. The ability of undercoordinated manganese species to activate gas-phase O_2 and facilitate the formation of a N-N bond are revealed to be instrumental to the outstanding catalytic performance. No deactivation is observed over 70 h on stream (**Fig. 1d**). CeO_2-supported isolated transition metals emerge as a novel class of materials for N_2O production, encouraging future studies to evaluate their potential in selective catalytic oxidations at large.

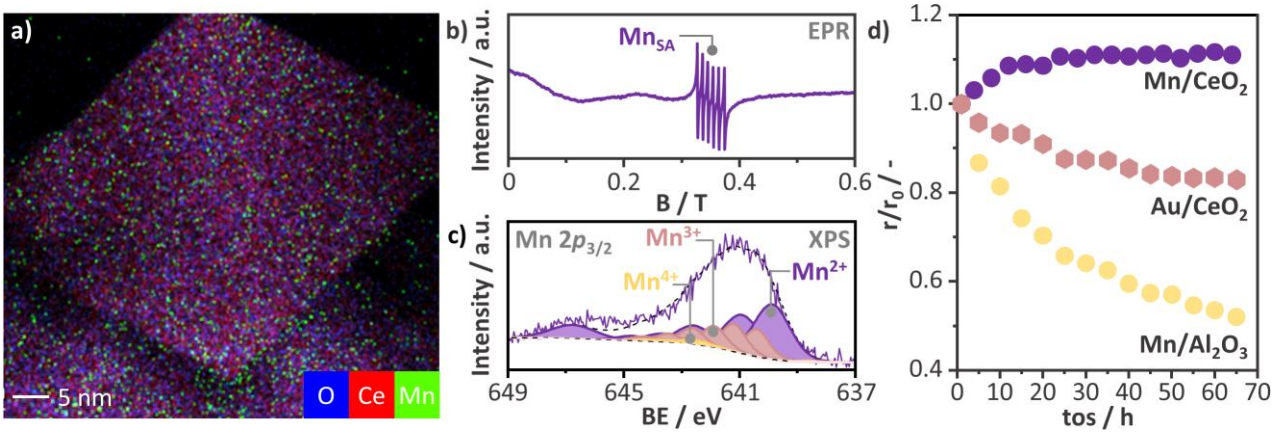

Figure 1. (a) Elemental map, (b) EPR and (c) XPS spectra of Mn/CeO_2. (d) Stability test of selected catalysts.

Acknowledgements
NCCR Catalysis, a National Centre of Competence in Research funded by the Swiss National Science Foundation.

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Bimetallic catalyst synthesis using galvanic displacement, electroless deposition methods and application for renewable chemical production

Weijian Diao[1*]
[1]*Villanova University, Villanova PA, United States*
[*]*Weijian.diao@villanova.edu*

Introduction. From petroleum refining to pharmaceuticals to automobile emission control, supported metallic catalysts are widely used in industrial processes and daily life. Bimetallic catalysts have been widely used in industrial processes which offer better performance of activity, selectivity and lifetime comparing to monometallic due to ensemble/geometric effects, electronic effects, and/or bifunctional effects. However, bimetallic catalysts are typically prepared on an industrial scale using either successive impregnation or co-impregnation methods which frequently provide inadequate control over placement of each metal with varying compositions and distributions of each metal [1].

Experimental/methodology. Using rational bimetallic synthesis methods including galvanic displacement (GD) and electroless deposition (ED) [2,3], different series of bimetallic catalysts including Pt-Ru, Pd-Au, Pd-Ag, Ag-Ir have been prepared with controllable composition and structure. Bimetallic catalysts synthesized by GD and ED methods have shown supreme performance for many different applications including selective hydrogenation reactions, selective oxidation reactions as well as direct methanol fuel cell. Detailed reaction mechanism study shows that precisely controlled bimetallic catalysts prepared by electroless deposition method significantly improve catalyst performance with ensemble/geometric effects, electronic effects, and/or bifunctional effects. In this study, metal precursors for Pd, Pt, Ir, Ag, Au and Cu were used for galvanic displacement (GD) and electroless deposition (ED) of secondary metal on primary metal. GD and ED liquid bath concentrations were measured using atomic adsorption spectroscopy (Perkin Elmer AAnalyst 900). Catalytic surface properties were obtained by XPS and H_2 chemisorption measurements using a Micromeritics ASAP 2920. XRD obtained from a Rigaku MiniFlex II and STEM images taken from a JEOL JEM-2100F were used for particle size measurements.

Results and discussion. Several series of bimetallic catalysts including Pt-Ru, Pd-Au, Pd-Ag, Ag-Ir have been prepared with controllable composition and structure with galvanic displacement (GD) and electroless deposition (ED) method. Surface coverage of secondary on primary metal varies from 5% to 97% based on chemisorption analysis. XPS, TPR, STEM and chemisorption indicated controlled bimetallic catalyst surface with strong metal-metal interactions. Bimetallic catalysts were tested for different applications including selective hydrogenation/oxidation, direct methanol fuel cell. With highly dispersed secondary metal and preciously controlled primary metal ensemble, significantly improve catalyst performance of activity, selectivity and stability were observed with ensemble/geometric effects, electronic effects, and/or bifunctional effects.

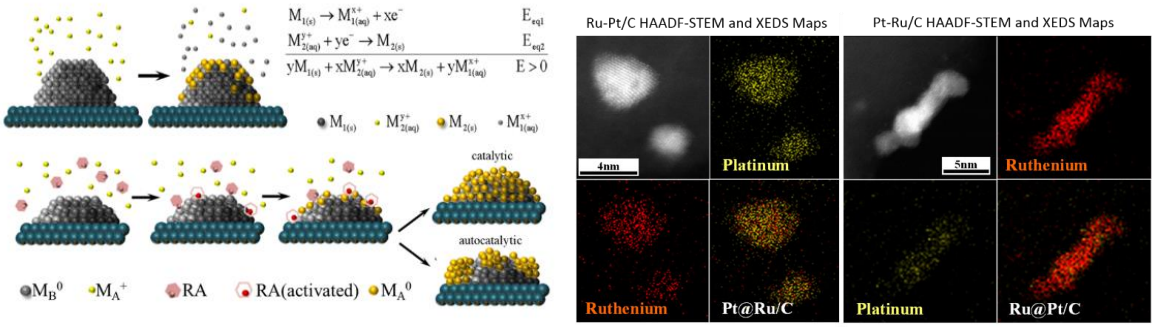

Figure 1. (A). Galvanic displacement (GD) and Electroless deposition (ED) methods; (B) HAADF-STEM of Ru-Pt and Pt-Ru bimetallic catalysts prepared by ED method [3].

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Cenospheres from fly ashes as catalytic supports of high application potential

P. Rybowicz[1], Y. Vitushynska[1], B. Samojeden[2], A. Łagosz[3], M. Motak[2], M. Michalik[4], A. Adamski[1*]

[1]*Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, PL 30-387 Krakow*
[2]*AGH-University of Science and Technology, Faculty of Energy and Fuels, Mickiewicza Ave. 30, PL 30-059 Krakow*
[3]*AGH-University of Science and Technology, Faculty of Material Science and Ceramics, Mickiewicza Ave. 30, PL 30-059 Krakow*
[4]*Jagiellonian University, Faculty of Geography and Geology, Gronstajowa 3a, PL 30-387 Krakow*
[*]*a.adamski@uj.edu.pl*

Introduction. As it can be shown basing on many representative examples, cenosphers extracted from fly ashes (generated worldwide in mass scale by energy sector) can be efficiently used in catalysis as supports or, after appropriate functionalization, also as composite catalytic materials. Their exploitation remains in agreement with main principles of circular economy, where a waste material from one industrial process can be successfully used (directly or after necessary valorization) as valuable material in another process. Cenospheres exhibit several interesting features making them particularly useful as catalytic supports. First of all, they are thermally stable as they were formed at temperatures exceeding 1200°C from non-flammable mineral components naturally occurring in coal. Cenospheres are rich in silicon, aluminum, iron, and alkali elements. On the other hand, cenospheres show relatively low specific surface areas. To overcome this disadvantage additional structural modifications are sometimes required. Our goal was to check whether commercial cenospheres can be used as suitable support materials for copper- and zinc-based catalysts for hydrogenation of CO_2.

Experimental/methodology. Commercial cenospheres of 150 and 300 μm in diameter (labelled hereafter as Cen-150 and Cen-300) have been impregnated with appropriate amounts of aqueous solutions of copper and/or zinc nitrates and then calcined at 400°C for 4 hours to obtain final catalytic systems. Both cenospheres and the supported oxide catalysts have been structurally (XRF, XRD, RS), texturally (SEM, porosimetry) and functionally (RS, DRIFT, UV-Vis/DR) characterized in detail.

Results and discussion. As it can be inferred from both XRD and RS results, interactions between cenosphere surfaces and the deposited phases are rather weak, favoring the formation of CuO and ZnO three-dimensional nanorystallites even at such low concentrations of the deposited phases as 0.5 mol. % of Cu or 0.3 mol. % of Cu and 0.2 mol. % of Zn. It was thus confirmed that cenospheres belong to the supports limiting natural tendency of the deposited oxide phases containing copper and zinc to expand. Simultaneously, as revealed by DRIFT, due to relatively many different stabilization sites ocurring on their surfaces, heterogeneity of surface hydroxyls stabilized on cenosphere-supported catalysts was distinctly strong. Moreover, our studies confirmed that cenosphere-supported oxide phases are stable and can be considered as useful catalytic materials for many reactions of environmental and technological importance, like e.g. hydrogenation of carbon dioxide.

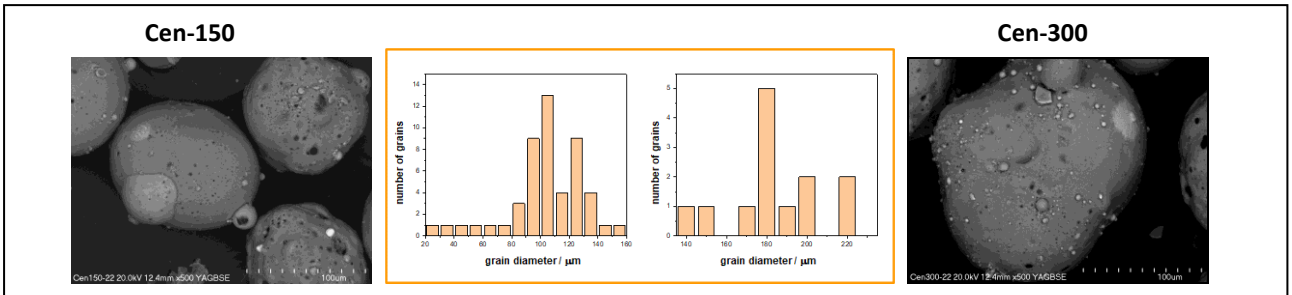

Fig. Morphological features of the studied cenospheres revealed by SEM/EDS analyses.

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Base catalysis of Lindqvist-type $[M_6O_{19}]^{8-}$ (M = Nb, Ta) clusters

S.Yamazoe,[1,2*] Y. Fujiki,[1] H. Nagakari,[1] V. Chudatemiya,[1] S.Kikkawa,[1] T. Matsuyama,[1] N.Nakatani[1]

[1] *Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Tokyo 192-0397, Japan.*

[2] *Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), Tokyo 102-0076, Japan.*

[*] *Yamazoe@tmu.ac.jp*

Keywords: metal oxide clusters, base catalyst, CO_2 fixation, super base

Introduction. Metal oxide clusters, called as polyoxometalates, have been widely used as acid and redox catalysts. Since Mizuno *et al*. reported the base catalysis of monooxotungstate $[WO_4]^{2-}$ [1] and polyoxotungstate $[HGeW_{10}O_{36}]^7$ [2], the base catalysis of metal oxide clusters has attracted much attention [3]. However, their basicity has not been yet studied systematically. Recently we found that polyanionic $[Nb_{10}O_{28}]^{6-}$ clusters acted as Brønsted and Lewis base catalysts [4,5]. In addition, the $[Nb_{10}O_{28}]^{6-}$ cluster was active for CO_2 fixation reactions to amine compounds. The large negative charges of surface oxygen atoms of M^V oxide clusters are expected to contribute to the base catalysis from density functional theory (DFT). In this study, we investigated the base catalysis of the metal oxide clusters using Knoevenagel, aldol condensation reactions, and CO_2 fixation reactions. We found that $[M_6O_{19}]^{8-}$ (M = Nb, Ta) clusters were active for acetone condensation reaction (pK_a = 26.5), which means that the $[M_6O_{19}]^{8-}$ are superbase. DFT calculation revealed that the Brønsted base sites are the bridged O sites on the cluster surface.

Experimental/methodology. tetrabutylammonium (TBA) salts of $[M_6O_{19}]^{8-}$ (TBA-M_6, M = Nb, Ta) were synthesized by a microwave-assisted hydrothermal method in tetrabutylammonium hydroxide aqueous solution according to the literature[4,5]. The fabricated clusters were characterized by ESI-MS, FT-IR, elemental analysis, and XAFS analysis, and the adsorption energy was calculated by DFT calculation. Base catalytic properties were evaluated by KC reactions, where nitrile compounds of different pK_a were reacted with benzaldehyde (BA) in DMSO at R.T. and 70°C under N_2 atmosphere. CO_2 fixation to styrene oxde (**SO**) was carried out in a batch-type reactor under atmospheric gas pressure. The reaction solutions were analyzed by GC-FID and GC-MS using an internal standard.

Results and discussion. The TBA-M_6 were characterized by elemental analysis, ESI-MS, UV-Vis, FT-IR, TG-DTA, and XAFS analyses. From the ESI-MS spectra, the signals assingend to $(TBA)_m(H)_n[M_6O_{19}]^{(8-m-n)-}$ were detected. In addition, the absorption bands characterized by the Lindqvist-type $[M_6O_{19}]^{8-}$ structure were observed in FT-IR spectra. These results indicate the synthesis of $[M_6O_{19}]^{8-}$. Next, the base strength of metal oxide clusters was tested by Knoevenagel condensation reactions. The TBA-M_6 clusters showed catalytic activities for the reaction of benzyl alcohol with 4-methoxybenzyl cyanide (pK_a = 23.8). In addition, the TBA-M_6 clusters were also active for acetone condensation reaction (pK_a = 26.5). The catalytic activities of TBA-Ta_6 were higher than those of TBA-Nb_6 for these reactions. DFT calculation revealed that the average negative charges of surface oxygen atoms of $[Ta_6O_{19}]^{8-}$ were higher than those of $[Nb_6O_{19}]^{8-}$[6]. The strong basisity of $[Ta_6O_{19}]^{8-}$ is due to the negativities of surface oxygen atoms. The proton adsorption sites were evaluated by DFT calculations using proton adsorption energy. The bridged O sites on the surface of the cluster is expected to be proton adsorption sites whereas the terminal O sites are most negatively charged and are expected to act as base sites[6]. In addition, Lewis base properties of TBA-M_6 were evaluated by CO_2 fixation reactions. CO_2 fixation reactions to noto only **SO** but also amino compounds proceeded over both catalysts although TBA-Ta_6 had higher conversion than TBA-Nb_6.

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Synthesis, characterization and purification of tailor-made polyoxometalate (POM) catalysts for catalytic applications via the lacunary anion $[PMo_9O_{34}]^{9-}$

Jan-Christian Raabe[1*], Maximilian J. Poller[1] and Jakob Albert[1]

[1]*Institute for Technical and Macromolecular Chemistry, Universität Hamburg, Bundesstraße 45, 20146 Hamburg, Germany*
[*]*JanChristian.Raabe@uni-hamburg.de*

Keywords: Synthesis, Characterization, Nanofiltration, Membranes, Polyoxometalates, Purification

Introduction. Polyoxometalate (POM) catalyst synthesis for RedOx catalytic applications proves to be extremely challenging, as the most suitable substitution metal and a suitable synthesis strategy must be found. From a synthetic point of view, difficulties often arise in finding the optimal synthesis conditions, e.g. pH value, right precursor compound, purification of the resulting raw product etc.[1] The latter is currently the biggest challenge in synthesis, since defined pH values are required during POM synthesis and the precursor compounds usually contain alkali metals. This leads to undesired salt formation. Since both the POM and the alkali salt are equally soluble in aqueous medium, an efficient purification is usually severely limited. In organic synthesis, column chromatographic purifications have proven to be the method of choice for product separation; however an equivalent method for the separation of purely inorganic compounds does not yet exist. Therefore, we present a POM synthesis strategy starting from a triple lacunary Keggin species, with which a maximum of three out of twelve metal positions can be occupied by foreign transition metals. Directly coupled to the synthesis approach, we present an efficient nanofiltration process on a nanoporous membrane as diafiltration process, with which the salts can be completely removed from the POM raw product.[2]

Experimental/methodology. The synthesis strategy is based on an *in situ* lacunary approach. Here, the species $[PMo_9O_{34}]^{9-}$ (LHPA-3) is synthesized starting from molybdate and phosphate precursors in acidic aqueous solution.[3] In the next step the vacancies of the lacunary anion are filled by adding foreign, RedOx active transition metal precursors [M] (Figure 1).[4]

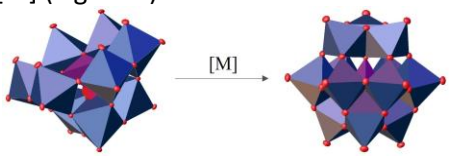

Figure 1: Filling of the vacancies with foreign transition metals results in a substituted Keggin-type structure.

The purification of the reaction solution (feed fraction) to remove unwanted salts is done by an nanofiltration process over four cycles in which the alkali salts are enriched in the permeate fraction and the POM in the resulting retentate fraction.[2]

Results and discussion. Using this approach we were able to incorporate different catalytically active transition metals into LHPA-3. All compounds were characterized spectroscopically and electrochemically. Furthermore, we could show that the incorporated transition metal has an influence on the whole electronic structure of the POM which causes a shift of the different RedOx processes, measured by electrochemical techniques. Our new developed nanofiltration process for desalination of POMs proves to be efficient since all POM elements seem to be rejected and the salts are removed completely.

Acknowledgments
We thank the Central Analytics Department of UHH for data collection and supporting our project.

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Potential uses in heterogeneous catalysis of newly synthesized polyacid-functionalized mesoporous materials

J. Schneider[1], J. Richard[1], A. Phimphachanh[1,2], P. Lacroix-Desmazes[1], M. In[2], Corine Gerardin[1], Nathalie Marcotte[1], Nathalie Tanchoux[1]*

[1]*ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France*
[2]*Laboratoire Charles Coulomb, Univ. Montpellier, Montpellier, France*
* *nathalie.tanchoux@enscm.fr*

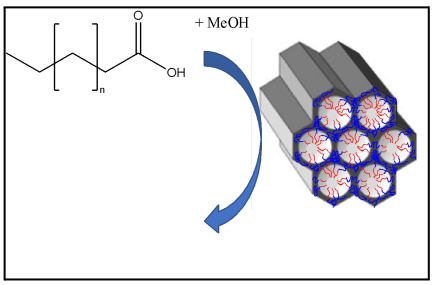
Keywords: Heterogeneous Catalysis / Functionnal Mesoporous materials / sol-gel chemistry

Introduction. Polymer-functionalized mesoporous silica materials combine the textural properties of mesoporous materials and the chemical properties of polymers. These two features make them excellent candidates for diverse applications such as catalysis. The synthesis of such hybrid materials is limited by the functionalization step; a high density of polymers and a homogeneous distribution of this polymer within the pores remain difficult to reconcile [1]. We present here the synthesis and first results on catalytic properties of polymer-functionalized mesoporous silica materials prepared by an innovative and versatile process based on polyion complex (PIC) micelles, the Mesopic process, which overcomes the issues of density and homogeneity of functionalization [2, 3].

Experimental/methodology. The Mesopic process consists in the formation of polyionic complexes (PIC) formed by electrostatic interaction between two hydrophilic polymers, namely (i) double-hydrophilic block copolymer : either a poly(poly(ethylene oxide)-methyl ether acrylate)-b-poly(styrene sulfonate) (PAPEO-b-PSS, bearing strong acid groups) or a poly(poly(ethylene oxide)-methyl ether acrylate)-b-poly(acrylic acid) (PAPOE-b-PAA, bearing weak acid groups) and (ii) an oppositely charged polyamine. During the sol-gel process, the PAPEO chains are anchored in the silica. The polyamines are then removed from the PIC assembly by pH stimulation, thus revealing the porosity and the weak/strong acidic functions. Materials are characterized by TEM, SAXS, TGA, ICP/MS, N_2 adsorption, and acid-base titration to determine the number of acid functions.

Catalytic materials bearing strong acid sites have been evaluated in the esterification of fatty acids by methanol. The experiments have been carried out in batch reactor using carboxylic acids going from hexanoic to palmitic acid in methanol at 60°C during the desired time. Catalytic materials bearing weak acid sites have been evaluated in the Mannich reaction using as substrates cyclohexanone, aniline and benzaldehyde in acetonitrile, in a btach reactor at 40°C during the desired time. Reaction products analysis was carried out using GC-MS and GC-FID.

Results and discussion. We first showed in both cases that despite the PAPOE chains not being covalentely bonded to the silica, the materials remain stable in catalytic conditions and the reaction media, i. e. methanol and acetonitrile.



We further showed that, in the case of esterification reaction, we could obtain conversion up to 20-30% comparable to what can be obtained using Amberlyst 15 catalysts, or for other sulfonic acid functionalized silicas.

The first experiments on weak acid catalysts in the Mannich reactions also exhibited good results, comparables to those precedently obtained by the group, using alginic acid heterogeneous catalysts [4].

These results evidence the great potential of such materials, synthesized by the Mesopic process, avoiding the costly calcination step, and they will be discussed in details during the conference.

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Shielding effect of mesoporous catalysts for plasma-enhanced catalytic synthesis of ammonia under ambient conditions

Y. Wang[1], X. Tu[1*]

[1]*Department of Electrical Engineering and Electronics, University of Liverpool, Liverpool, L69 3GJ, UK*
[*]*Corresponding author: xin.tu@liverpool.ac.uk*

Keywords: Non-thermal plasma; Plasma catalysis; Ammonia synthesis; Mesoporous catalysts; MCM-41.

Introduction

Plasma catalysis is a promising technology for decentralized small-scale ammonia (NH_3) synthesis under mild conditions using renewable energy and shows great potential as an alternative to the conventional Haber-Bosch process[1]. To date, this emerging process still suffers from a low NH_3 yield due to limited knowledge in designing highly efficient catalysts and the in situ plasma-induced reverse reaction (i.e., NH_3 decomposition). Here we show that a bespoke design of supported Ni catalysts using mesoporous MCM-41 could enable efficient plasma-catalytic NH_3 production at 35 °C and 1 bar with >5% NH_3 yield at 60 kJ/L. Specifically, the Ni active sites were deliberately deposited on the external surface of MCM-41 to enhance plasma-catalyst interactions and hence improve NH_3 production. The desorbed NH_3 could then diffuse into the ordered mesopores of MCM-41 to be shielded from decomposition due to the absence of plasma in the mesopores, that is, shielding protection, thus driving the reaction forward effectively. This strategy sheds light on the importance of a rational design of catalysts specifically for improving plasma-catalytic processes[2].

Experimental/methodology

Plasma-catalytic NH_3 synthesis was conducted in a coaxial dielectric barrier discharge (DBD) plasma reactor with circulating water as the ground electrode, which can maintain a reaction temperature of 35 ^{o}C during the reaction. The DBD reactor was connected to an AC high-voltage power supply with a peak voltage of up to 25 kV. The discharge power was controlled between 16 and 40 W, and the frequency was fixed at 9.2 kHz.

Results and discussion

Compared to the plasma alone, packing the DBD reactor with SiO_2 or MCM-41 supports enhanced the ammonia synthesis rate (R_{NH3}), i.e., 575 µmol/g/h (plasma alone) vs. 1131 µmol/g/h (with SiO_2) and 1452 µmol/g/h (with MCM-41). The comparatively high R_{NH3} value of the plasma-MCM-41 system could be ascribed to the highly porous structure of MCM-41 compared to SiO_2. As expected, loading Ni onto either SiO_2 or MCM-41 enhanced the R_{NH3} significantly, proving the active role of metallic Ni in ammonia synthesis. Again, the Ni/MCM-41 catalysts were more active than Ni/SiO_2 with the following activity order: Ni/MCM-out > Ni/MCM-both > Ni/MCM-in > Ni/SiO_2. In particular, Ni/MCM-out exhibited a high NH_3 yield of about 3.7%, which was ~8 times higher than that of the plasma alone. Furthermore, the plasma-catalytic system using Ni/MCM-out displays very promising performance (at a low flow rate of 40 mL/min) with a high NH_3 yield (5.3%) and concentration (27115 ppm) at an energy yield of 1.2 gNH_3/kWh. The energy yield of the Ni/MCM-out system could be improved to 3.9 gNH_3/kWh by increasing the flow rate to 1.2 L/min, but this operation compromises the ammonia concentration. To illustrate this enhancement of NH_3 yield using mesoporous catalyst, we have developed a unique integrated plasma/FTIR cell for *in situ* probing of plasma-induced surface reactions over different Ni/MCM-41 catalysts, together with comprehensive catalyst characterization and plasma diagnostics, to clearly demonstrate and elucidate this new strategy for enhanced plasma-catalytic ammonia synthesis under ambient conditions with solid and convincible evidence.

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Morphological tuning of perovskite-type oxides for enhanced catalytic activity

H. Drexler[1,2], J. Rollenitz[1,2], F. Schrenk[1,2], L. Lindenthal[1,2], C. Rameshan[1,2*]

[1]*Chair of Physical Chemistry, Montanuniversität Leoben, Austria*
[2]*Institute of Materials Chemistry, TU Wien, Austria*
[*]*christoph.rameshan@unileoben.ac.at*

Keywords: tailored surfaces, exsolution, nanoparticles, perovskite oxides, reverse water-gas shift reaction

Introduction. In the field of CO_2-utilization, perovskite-type oxides are promising catalysts for the CO_2-activation e.g., via the **r**everse **W**ater-**G**as **S**hift reaction (rWGS) [1, 2]. The ABO_3 structure of these materials allows for tailored properties such as enhanced catalytic activity and selectivity, as certain metal compositions trigger *in-situ* nanoparticle exsolution of the B-site elements (e.g., Co, Fe, …) under reducing conditions [3]. Hereby, the transition metals migrate from the lattice to the surface, forming uniformly distributed, stable, and catalytically active metallic nanoparticles, anchored in the perovskite support.

Experimental/methodology. Several Pechini sol-gel protocols for perovskite-type oxides are known [4], but their influence on the resulting material is not always comprehensible. By varying the synthesis conditions through changing the pH and/or adding different additives/complexing agents, the impact on the catalyst **N**d$_{0.6}$**C**a$_{0.4}$**F**e$_{0.9}$**Co**$_{0.1}$O$_3$ (NCF-Co) was investigated. The materials were analysed and compared via **X**-**R**ay **D**iffraction (XRD) and **S**canning **E**lectron **M**icroscopy (SEM), in addition to **T**emperature **P**rogrammed **R**eduction measurements (TPR). Surface areas were determined using the **B**runauer–**E**mmett–**T**eller method (BET) [5]. The exsolution process was monitored in regards to on-set temperatures and the size of the particles after rWGS reaction.

Results and discussion. Most synthesis variations resulted in phase-pure catalyst materials, displaying different surface morphologies (Fig. 1) and areas. Not all methods could enhance the catalytic activity, preliminary results suggest that a combination of elevated pH and additives, such as ethylene glycol, might be most promising in regards to enhanced catalytic activity.

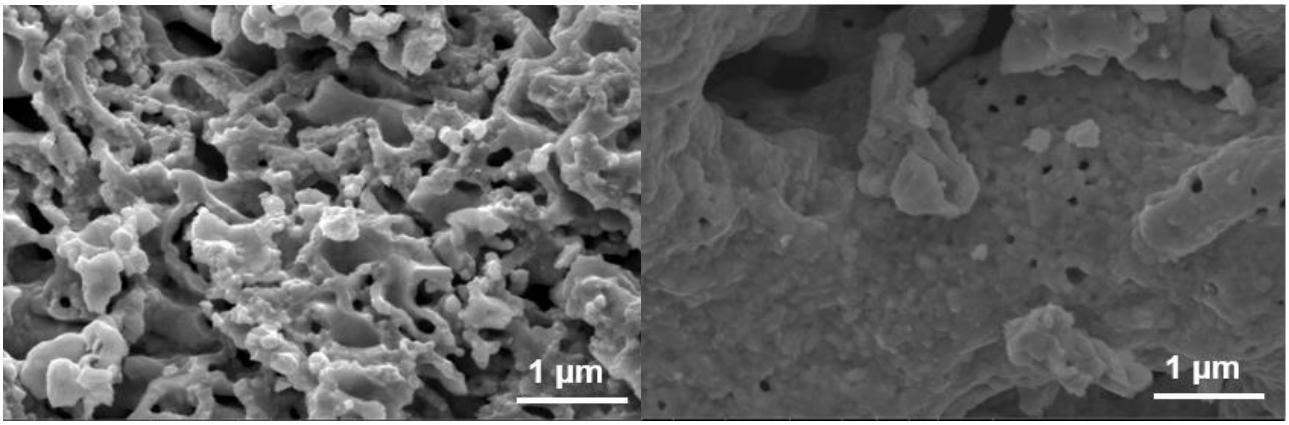

Fig. 1: SEM images of Nd$_{0.6}$Ca$_{0.4}$Fe$_{0.9}$Co$_{0.1}$O$_3$, using modified Pechini sol-gel methods: pH 1 and addition of ethylene glycol and citric acid (4:1 ratio, left), adjusted to pH 3 with ammonia (right).

Acknowledgments
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Lewis acid zeolites by regioselective manipulation of germanosilicates

M. Shamzhy*, J. Zhang, S. Abdi, J. Čejka

Charles University, Prague, Czech Republic
**mariya.shamzhy@natur.cuni.cz*

Introduction. Zeolites are porous crystalline solid acid catalysts that are widely used in the petrochemical industry and have a high potential for new applications. A particularly interesting class of zeolites includes germanosilicates. Although the use of germanosilicates in catalysis is strongly limited by their weak acidity and low hydrothermal stability, the enhanced lability of Ge-O vs. Si-O bonds and the regioselective location of Ge atoms in certain framework positions make them ideal starting materials for rational top-down synthesis of catalysts with tunable functionalities and structures [1]. To tailor Lewis acid catalysts with variable metal sites, we have developed post-synthesis isomorphous substitution of Ge with different tetravalent elements coupled with Ge recovery and recycling [2]. In addition, we have produced a unique set of Lewis acid zeolites with monotonically changing micropore sizes when combining a controllable size reducing of Ge-enriched structural units and the incorporation of framework tetravalent elements [3].

Experimental/methodology. IWW, IWR, UOV, and UTL zeolites of different chemical compositions were hydrothermally synthesized and further subjected to different postsynthesis modifications (e.g., isomorphous substitution with tetravalent elements or Assembly-Disasembly – Organisation – Reassembly [1]). The resultant catalysts were thoroughly characterized using X-ray diffraction, physisorption, electron microscopy, chemical analysis, and IR, NMR, and UV-VIS spectroscopies. The Ti-containing catalysts were tested in the epoxidation of alkenes, while Sn- and Zr-substituted ones were assessed in the Meerwein-Ponndorf-Verley (MPV) reduction of aldehydes.

Results and discussion. By optimizing the degermanation conditions, up to 94 % of Ge was recovered from zeolites of different structures and further recycled in their hydrothermal synthesis. Subsequent metalation of degermanated materials resulted in a set of Ti-, Sn-, and Zr-substituted IWW and UTL catalysts outperforming hydrothermally synthesized zeolites of the same structure in the epoxidation of 1-octene and MPV reduction of furfural. This result is explained by a higher concentration of framework metal sites achieved when using the top-down vs. bottom-up synthesis approach.

The combination of Ti or Sn incorporation and rearrangement of Ge-enriched structural units in the IWW, IWR, UTL and UOV frameworks resulted in a series of Lewis acid zeolites with controllable structures and micropore sizes. Diffraction and microscopy analyses verified the structural characteristics of the daugther materials, while IR spectroscopy using adsorbed probe molecules (pyridine, d_3-acetonitrile) evidenced the existence of different framework four-valent metal coordination environments (‘closed’ and ‘open’ sites). Control over the structural and acidic characteristics of designed zeolites allowed us to address their property-function relationships. In 1-hexene and cyclohexene epoxidation, the conversion of reactants and selectivity towards the targeted epoxides gradually decreased with micropore size of Ti-containing zeolites. In contrast, in MPV-reduction of citronellal, higher selectivity to the targeted product was achieved over daughter Sn-substituted zeolites with a smaller reaction space around acid centers compared to the parent stannogermanosilicates. In summary, the proposed synthesis approach that utilizes both structural and chemical modification of germanosilicates provides the tool for better control over the characteristics of zeolite catalysts.

Acknowledgments

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A study of effect of the Ti loading on the reaction rate and of post-treatment of ammoximation of cyclopentanone using TS-1 as catalyst

A.Orozco-Saumell[1*], I. Martínez-Salazar[1], J. M. Jiménez-Martín[2], J. Iglesias Morán[2], R. Mariscal[1] and M. López Granados[1]

[1] *Sustainable Energy and Chemistry group (EQS Group), Institute of Catalysis and Petrochemistry (CSIC), C/ Marie Curie. 28049. Madrid. Spain.*

[2]*Chemical and environmental engineering group. ESCET. University Rey Juan Carlos, C/ Tulipan s/n. 28933. Mostoles. Madrid. Spain.*

[*]*ana.o.s@csic.es*

Keywords: Ammoximation, cyclopentanone, cyclopentanone oxime, TS-1

Introduction. Nylon 6 is currently an oil-derived polymer whose production encompasses the reaction of cyclohexanone with hydroxylamine to render cyclohexanone oxime, its further Beckmann rearrangement to caprolactam and the subsequent polymerization to Nylon 6. A very sustainable route to produce Nylon has recently been industrially implemented that involves the in-situ synthesis of hydroxylamine by the catalytic oxidation of ammonia with H_2O_2 in the presence of Titanium Silicalite zeolite (TS-1) that reacts with cyclohexanone yielding the oxime.[1] Interestingly, Nylon 5 could be produced from cyclopentanone (CPONE) following the same sustainable reaction route developed for Nylon 6, the H_2O_2/NH_3 ammoximation of CPONE, Beckmann rearrangement to the lactam (δ-valerolactam) and polymerization to Nylon 5.

Experimental/methodology. A series of parent TS-1 catalysts with different Ti loading was prepared using a modified dried sol-gel conversion protocol. This methodolgy results in a low usage of TPAOH while still yielding TS-1 crystallites with dimensions of a few hundred nm. Larger crystallite size prevents the access of the solution to the inner part of the crystallite. Additionally, aiming at improving the activity, a TS-1 prepared with an initial ratio of Ti/S= 0.12 during the preparation was further modified by post-treatment of this parent TS-1 with TPABr and ethylamine (EA).

Results and discussion. The ammoximation of cyclopentanone to cyclopentenone oxime has been studied using a series of zeolites and mesostructured silica with different heteroatoms and structures. Because the best catalytic activity was that of TS-1, a series of catalyst varying amounts of Ti was synthesised and characterised by chemical analysis, XRD), N_2 adsorption, deuterated acetonitrile chemisorption, UV-VIS spectroscopy and XPS. It was found that the intrinsic rate per Ti site (TOF number) in TS-1 catalysts strongly depends on the Ti loading, showing a volcano type curve (Fig. 1). Additionally it was observed that the simultaneous postreatment of TS-1 with TPAOH and EA results in a substantial increase of the TOF that was explained by the creation of new Ti species (such as $Ti(OSi)_3OH$ and $Ti(OSi)_2(OH)_2(H_2O)_2$).

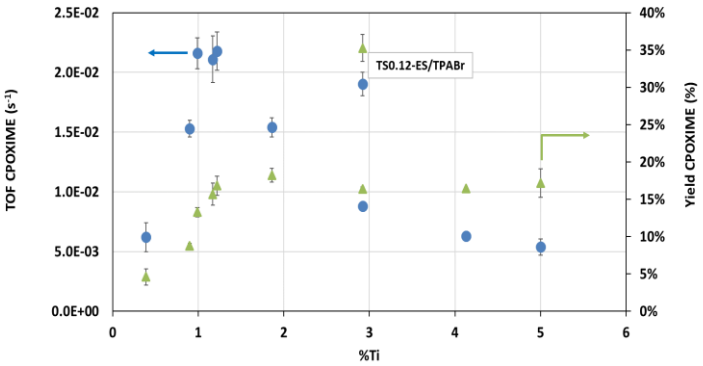

Figure 1. Study rate of reaction of as-prepared samples. Reaction conditions: 0.5 h of reaction time (except for T/Si= 0.003 that is 2 h), 70 °C, 1 wt % catalyst, 5 wt % of cyclopentanone, 85 % t-BuOH/H_2O, H_2O_2/CPO and NH_3/CPO mol ratio of 1.2.

Acknowledgments

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Aluminophosphate CIT-16P Having Distorted Erionite Structure and Methanol-to-Olefins Behavior of Its Transformation Product SAPO-17

Jong Hun Kang[1*], Faisal H. Alshafei[2], Sung June Cho[3], Mark E. Davis[2]

[1]*School of Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea 08826*
[2]*Chemical Engineering, California Institute of Technology, Pasadena, California, USA 91125*
[3]*Department of Chemical Engineering, Chonnam National University, Gwangju, Republic of Korea 61186*
******jonghunkang@snu.ac.kr*

Keywords: Silicoaluminophosphate, CIT-16P, SAPO-17, 3D-3D Transformation, Methanol-to-olefins

Introduction. The methanol-to-olefins (MTO) process uses small-pore silicoaluminophosphate (SAPO) molecular sieves with lower acid strength than isomorphous zeolite counterparts to convert methanol. The selectivity of light olefins (ethylene, propylene, and butylenes) is primarily determined by the cage topology [1] and acid site density [2] of the used small-pore molecular sieves. This study presents a new SAPO material, CIT-16P, that transforms to SAPO-17 and produces more propylene than ethylene in MTO reaction, supporting our theory of acid site density in erionite-type molecular sieves. [2] Results of CIT-16P-derived SAPO-17 are also compared to those of the recently-reported isomorph ECNU-38P. [3]

Experimental/methodology. Bisquinuclidinium-butane (DiQ-C_4) was used as the organic structure-directing agent (OSDA) for CIT-16P. The best gel composition and hydrothermal condition for CIT-16P was 0.04 SiO_2 : 0.47 Al_2O_3 : 0.45 P_2O_5 : 0.29 DiQ-C_4-$(OH)_2$: 40 H_2O at 190 °C, 72 hours. The transformation of the framework into SAPO-17 was achieved by removing OSDA from as-made CIT-16P. The MTO reaction tests were performed at 400 °C with a weight-hourly space velocity of 1.3 h^{-1} of methanol in a fixed-bed reactor.

Results and discussion. The ideal crystallization conditions for CIT-16P were found in the vicinity of those for SAPO-17 (ERI) and SAPO-56 (AFX). The transformation of CIT-16P into SAPO-17 was indicated by the change of the powder X-ray diffraction (PXRD) patterns before and after the removal of occluded OSDA. The Rietveld refinement of the PXRD pattern of as-made CIT-16P revealed that it is entirely composed of distorted cancrinite composite building units stabilized by the presence of occluded OSDA and the extra oxygen site (Figure 1, left) confirmed based on the solid-state ^{27}Al NMR spectrum. In the MTO reaction at 400 °C, SAPO-17 derived from CIT-16P produced more propylene than ethylene (E/P ~ 0.66, Figure 1, middle), which contradicts our cage-defining ring theory [1] for MTO selectivity distribution. The low Si content (Si/T ~ 0.02) of the parent CIT-16P may be responsible for this low E/P ratio, which results in sluggish formation of aromatic intermediates (Figure 1, right). [2] Also, CIT-16P showed a longer catalytic lifetime and higher conversion than ECNU-38P-derived SAPO-17 [3] due to its lower external acid sites.

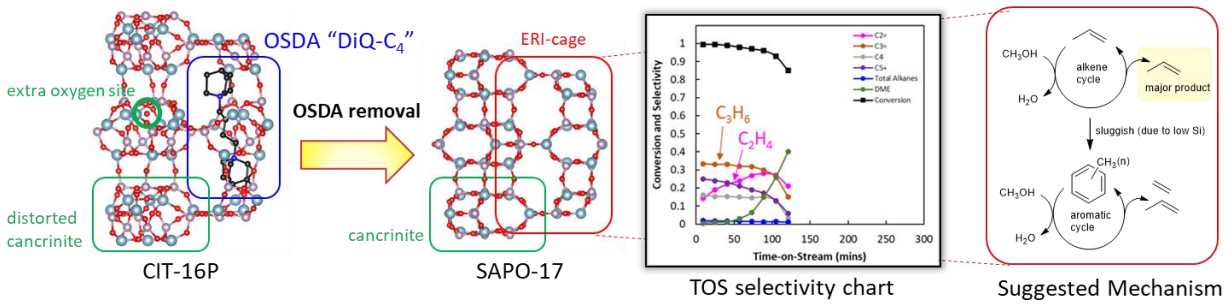

Figure 1. (left) Transformation of CIT-16P into SAPO-17, (middle) MTO time-on-stream olefin selectivity chart, and (right) suggested MTO mechanism within a low-Si ERI cage

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Hidden limitations: lactate synthesis over Sn-BEA zeolites with record Sn contents synthesized by a novel bottom-up strategy

Gleb Ivanushkin[1], Michiel Dusselier[1*]

[1]*Center for Sustainable Catalysis and Engineering CSCE, KU Leuven, Faculty of Bioscience Engineering, B-3000 Leuven, Belgium*
[*]*michieldusselier@kuleuven.be*

Keywords: Lewis acid catalysis, Sn-BEA, biomass conversion, methyl lactate, zeolite synthesis

Introduction. A key challenge for the chemical industry is the efficient and selective conversion of substrates derived from biomass. For the last two decades, Sn-BEA zeolites have emerged as first-class Lewis acid catalysts for a variety of biomass-related reactions: isomerization and epimerization of sugars [1], Baeyer-Villiger oxidation [2], and Meerwein-Ponndorf-Verley reduction [3]. Furthermore, the chemical route of producing lactic acid and alkyl lactates from carbohydrates using heterogeneous Lewis catalysts has great potential since low-cost purification and reduced (salt) is implied in the technology [4]. Nowadays, attaining high metal loadings in Sn-BEA catalysts is only possible through the post-synthetic approach, which is limited by the inherited properties of the parent zeolite. Here, by using a novel hydrothermal synthesis procedure, we were able to synthesize a series of Sn-BEA zeolites, among which one with the highest ever reported Si/Sn (final material) ratio of 14. This ratio has never been obtained in hydrothermal synthesis. On top, we have run catalytic conversions of 1,3-dihydroxyacetone (DHA) to methyl lactate (ML) and compared these results with the widely described Sn-BEA-F made via the fluoride approach (and with less Sn).

Experimental/methodology. The synthesis of the new Sn-BEA is the subject of a patent application and will be detailed in the talk, but it involves a new reactor type and a hydroxide media environment. Catalytic tests at low temperature (80°C) of DHA in methanol to ML were performed in 10 mL thick-walled glass reactors placed in a preheated block. Generally, 112.6 mg of DHA, 80 mg of catalyst, 60 mg of naphthalene, and 5.0 mL of methanol were added in the glass reactor, put in the block, and vigorously stirred for the required time, followed by rapid chilling in an ice bath for sampling. For high-temperature reactions (>100°C), a closed stainless steel reactor with a sampling valve was used. After the reaction, products were quantified through GC-FID analysis using a calibration curve.

Results and discussion. A Sn-BEA zeolite series with a wide Si/Sn ratio variation of 14-200 was synthesized. For benchmarking, a sample of Sn-BEA-F (classic fluoride approach) was made with Si/Sn 160. For all materials, phase purity was verified with PXRD, while crystallinity, surface area, and micropore volume were calculated from N_2-physisorption. Crystal size, heteroatom distribution, and chemical composition of synthesized zeolites were determined by TEM EDX and confirmed by ICP-AES. Moreover, the amount of Lewis acid sites was determined by FT-IR of absorbed CD_3CN as a probe molecule. The evaluation of catalytic data suggests that the Sn-BEA zeolite with Si/Sn 14 demonstrates 3-fold improved productivity after one hour of reaction versus the comparison sample. Based on the Arrhenius plot in a wide temperature range, very similar apparent activation energies were established (64 kJ/mol for both materials), which corresponds to the literature [5]. We have evidence that both samples undergo mass transport limitations: we surmise Sn-BEA-F has classic diffusion limitations occurring due to long-distance diffusion in the large crystals (10 µm), while the extreme concentration of Lewis sites cannot be efficiently supplied by enough diffusing reactants in the small-crystal Sn-BEA Si/Sn 14 (200 nm).

Acknowledgments
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Organic alkalis as an alternative for eco-friendly mechano-chemical synthesis of Layered Double Hydroxides-type catalysts

O.D. Pavel[1], B.-C. Jurca[1], R. Zăvoianu[1], R. Bîrjega[2], B. Cojocaru[1*], V.I. Pârvulescu[1*]

[1]*University of Bucharest, Faculty of Chemistry, Bucharest, 030018, Romania*
[2]*National Institute for Lasers, Plasma and Radiation Physics, PO Box MG-16, 077125 Măgurele, Romania*
[*]*Corresponding Author's E-mail address bogdan.cojocaru@chimie.unibuc.ro; vasile.parvulescu@chimie.unibuc.ro*

Keywords: organo-alkalis taylored LDH, condensation and aldol addition reactions

Introduction. Solid bases received a pretty high importance in the catalytic field due to their well-known advantages of non-corrosive and easier product separation for a a variety of domains [1] including environmental protection or fine chemistry. Among these, hydrotalcites-type materials (LDH) continue to elicit a great interest for catalysis owing to their specific properties. Further, the replacement of the alkaline cation with organic alkalis may offer a more viable alternative also avoiding the contamination of the product [2]. Based on this state of the art, the aim of this study was to re-visit LDH structures prepared in the presence of TMAOH (Tetramethylammonium Hydroxide) or TBAOH (Tetrabutylammonium Hydroxide) and to evaluate these materials in the synthesis of 3-ethoxypropionitrile by aldol addition and 2,6-dicyclohexylidene-cyclohexanone by Claisen-Schmidt condensation.

Experimental/methodology. The synthesis of LDH was carried out in a Mortar Grinder at a rate of 100 rot·min^{-1} for 1 h at a pH of 10 at RT taking quaternary salts as hydrolysis agents. For comparison, nitrates were as well co-precipitated from corresponding solutions, both with inorganic/organic bases. All the resulted solids were washed until a neutral pH, dried at 120 °C for 24 h and further calcined at 460 °C for 18 h. The samples were structurally characterized by XRD, DRIFT, BET, DTA-TG, and TEM. Their basicity was evaluated from the irreversible adsorption of acrylic acid (pK_a = 4.2) and phenol (pK_a = 9.9). The catalytic reactions were carried out in batch conditions following a continuous evaluation of the yield.

Results and discussion. Claisen-Schmidt condensation and the synthesis of 3-ethoxypropionitrile require catalysts with different basicities [3]. For the Claisen-Schmidt condensation the addition of Zn or Y to the Mg-Al-LDH in loadings below 15 % led to an increase of the basicity (higher for Zn) that corresponded to an increase of the conversion with almost 14% compared to the parent LDH. Noteworthy, the selectivity in the 2,6-dicyclohexylidene-cyclohexanone product was total. No benzoic acid as by product due to the oxidation of benzaldehyde has been detected.

The basicity was as well influenced by the organic base utilized in the construction of the LDH. TBAOH which has an increased basicity compared to TMAOH generated a more basic catalyst and, in acordance, the conversion of cyclohexanone to the dicondensate compound on this LDH was 10% higher.

On the other side, the comparison of Li-Al and Mg-Al-Y LDH indicated an enhanced basicity of the LDH with Y (four times higher) compared to the catalysts with Li. Correlated to this, the activity of the Mg-Al-Y LDH in the synthesis of 3-ethoxypropionitrile was three times higher.

Recycling the catalysts five times occurred with no change in the catalytic behavior thus demonstrating a very good stability, also confimed by the investigated characterization techniques.

Acknowledgments

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Porous Organic Semiconductors: Synthesis and Heterogeneous Photocatalysis

Tomaž Kotnik[1], Albin Pintar[1], Gregor Žerjav[1], and Sebastijan Kovačič[1]*

[1] *Department of Inorganic Chemistry and Technology, Laboratory for catalysts, National Institute of Chemistry Hajdrihova 19, SI-1001 Ljubljana.*

**tomaz.kotnik@ki.si and sebastijan.kovacic@ki.si*

Keywords: organic semiconductors, Knoevenagel condensation, Schiff-base condensation, Staudinger reaction, photocatalysis.

Introduction.

Organic semiconductors, particularly conjugated polymers (CPs), have shown exceptional optoelectronic properties and are being explored for commercial applications, such as organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs). Conjugated porous polymers (CPPs), on the other hand, are materials that combine the optoelectronic properties of their non-porous congeners, i.e., CPs, with high porosity and lightweightness.[1] As such, they have shown promise as catalysts for photocatalytic transformations. However, metal-catalyzed reactions are usually used for their synthesis, e.g., Suzuki, Sonogashira, or Yamamoto, which poses a certain risk for (waste) water remediation since metallic catalyst residues can enter the water and contaminate it.[2] Therefore, there is great interest in metal-free polycondensation reactions for the synthesis of organic semiconductors for heterogeneous catalysis.

Experimental/methodology.

In this study, different transition-metal-free reactions such as Knoevenagel, Schiff-base, or Staudinger reactions were used to prepare highly porous π-conjugated foams by soft-templating, which were characterized in detail using solid-state NMR and FTIR spectroscopy, elemental analysis, diffuse reflectance spectroscopy (DRS), photoluminescence (PL), and cyclic voltammetry (CV). These highly porous foams were then evaluated for their photocatalytic performance in the sulfoxidation of methyl phenyl sulfide and degradation of model organic pollutants in water.

Results and discussion.

For the first time, organocatalyzed reactions (i.e., Knoevenagel, Schiff-base, or Staudinger reactions) and soft templates (i.e., emulsions or foams) were combined to obtain highly porous π-conjugated foams.[3,4] The special optoelectronic properties of these foamy photocatalysts enable them to efficiently catalyze a model sulfoxidation reaction or the degradation of aniline dissolved in water under visible light.

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Photocatalytic properties of COK-47, a versatile Ti (IV)-MOF for visible light driven hydrogen evolution reaction

Pablo Ayala[1*], S. Naghdi[1], S.P. Nandan[1], J. Rath[1], S. Myakala[1], B. Fickl[1], H. Saito[2], M. Caspary Toroker[3], A. Cherevan[1], D. Eder[1]

[1]*Vienna University of Technology, Vienna, Austria*
[2]*Kyushu University, Fukuoko, Japan*
[3]*Israel Institute of Technology, Haifa, Israel*
[*]*pablo.ayala@tuwien.ac.at*

Keywords: metal organic frameworks, visible light absorption, hydrogen, water splitting, titanium SBU

Introduction. The world's growing need for renewable energy sources make it imperative to find sustainable and green fuels, e.g. hydrogen (H_2). However, photocatalytic water splitting for H_2 production is still a challenging reaction for ordinary metal-oxide-based catalysts.[1] Metal-organic frameworks (MOFs) are porous and crystalline materials that have been widely investigated by the scientific community in recent years and show excellent properties as photocatalysts. In this regard, Ti-based MOFs are particularly interesting because their photo-responsive behavior promotes H_2 evolution reaction (HER), one of the half reactions for water splitting.[2] A newly described and photoactive Ti-MOF with 2D secondary building units (SBUs) and a biphenyl organic linker has caught our attention due to its unique structure and promising composition for enhanced light absorption.[3]

Experimental/methodology. In this contribution, we investigate the photocatalytic properties of *COK-47* towards HER under diverse light sources and compare it to benchmark Ti-based MOFs. We have replicated the original syntheses reported by Smolders[3], yielding two materials: COK-47_{Small} and COK-47_{Large}. We have also come up with a new and simplified synthesis procedure using titanium(IV) tetraisopropoxide (TTIP) and biphenyl-4,4'-dicarboxylic acid (BPDC) as precursors in a DMF/MeOH mixture. The mixture is heated using microwave (MW) irradiation for 1h and after filtration, milling and drying, COK-$47_{\mathbf{New}}$ is obtained. All materials were thouroughly investigated in terms of their structure and morphology (XRD, TEM), connectivity and state (FTIR, Raman, XPS), surface area and missing ligand defects (N_2-physisorption and TGA) and optoelectronic properties (PL, TRES, DFT). Finally, their photocatalytic performance towards hydrogen evolution reaction was tested.

Results and discussion. We did a first-time detailed investigation on the optoelectronic and photocatalytic properties towards HER of COK-47. This new MOF is highly active in both UV and visible (with 29.5 and 8.6 $\mu mol\ h^{-1}$), setting it amongst the most active MOFs for – especially visible light driven – HER.

We were also able to identify the impact of defects and surface area on the activity and unraveled important insights on the reaction mechanisms of different sacrificial agents. Our data strongly suggests a ligand to metal charge transfer mechanism (LMCT), which, in combination with the 2D SBUs, allows for an efficient charge separation and extraction process.

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Structure Engineering Steer the Photocatalytic Activity of Carbon Nitride in Organic Synthesis

M. Melchonna[1*], P. Fornasiero[1], G. Filippini,[1] M. Marchi,[1] F. Longobardo,[1] E. Raciti,[2] S.M. Gali,[2] A. Actis,[3] E. Salvadori,[3] C. D'Agostino,[4] L. Forster,[4] D. Lee,[4] D. Beljonne,[2] M. Chiesa,[3] R. Lazzaroni,[2] M. Prato,[1]

[1]*Dept. of Chemical and Pharmaceutical Sciences and INSTM Trieste Research UNITS, University of Trieste, via L. Giorgieri 1, 34127 Trieste, Italy*
[2]*Laboratory for Chemistry of Novel Materials, Materials Research Institute, University of Mons-UMONS, Mons, Belgium*
[3]*Dept. of Chemistry and NIS Centre, University of Torino, Via Pietro Giuria 7, 10125 Torino (Italy)*
[4]*Dept. of Chemical Engineering, The University of Manchester, Oxford Road, Manchester M13 9PL, UK.*

[*]*Corresponding Author's melchionnam@units.it*

Keywords: photocatalysis, organic synthesis, carbon nitride

Introduction. The *ad hoc* post-synthetic structural modification of graphitic carbon nitride (g-CN) offers a pathway for triggering a large range of organic reactions with a considerable increase of photocatalytic efficiency. As demonstrated both exeprimentally and theoretically, such improved efficiencies are the result of a better suited interaction between the CN surface and the reacting substrates.

Experimental/methodology. Various types of modification were carried out on the pristine g-CN for the specific photocatalytic organic C-X coupling (X = C, N, O, S). Amorphization and reduction (am-CN and red-CN) were performed by subjecting the g-CN to thermal treatiment under argon and hydrogen/argon flow respectively. Carbon vacancies were introduced by means of microwave irradiation (mw-CN).

Results and discussion. The pristine g-CN prepared by the melamine precursor was used as a starting platform and as the benchmark catalyst for the various photocatalytic organic reactions. The first target reaction was the C-C coupling between perflruoroalkyl compounds and halogenated electron rich substrates, where highest activities were observed with the am-CN photocatalyst, which showed a 5-fold higher activity as compared to g-CN.[1,2] By means of detailed structural charaterization and advanced ^{15}F NMR studies, the higher activity was partly related to the improved halogen-bonding between the structure of am-CN and the halogenated reagent. Moreover, given the radical mechanism of the reaction, DFT calculations [3] and EPR experiments [4] revealed the importance of defective domains and radical distributrion. The Ni-based dual photoredox catalysis was next explored for the C-X coupling of a variety of substrates, and it emerges that the mw-CN was by far the best photocatalyst. In this case, the more complex catalytic mechanism and the most critical structural parameters that defined the activity trends were discovered through a comprehensive investigation of the structure activity realtionship with various advanced methods of charaterization employing XPS, EPR, nanoIR, solid state NMR, HRTEM. It was found that the formation of C vacancies in the g-CN was instrumental to harness the CN-Ni binding and elecrtron transfer, thanks to the formation of either triazole moieties or imine/amine sites able to bind Ni to form a squre planar complex. DFT computational methods highighted the differences in energies of the possible complexes as well as the charge transfer dynamics. The catalysis exhibited a large scope with good to excellent activities, and a production rate for the model reaction that exceeded that of other benchmark photocatalysts.

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Plasmonic Cu_2SSe Nanocrystals: Chemical Synthesis and Applications

N. R. Manwar[1*], J.C. Colmenares[1*]

[1] *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.*

[*] *Corresponding Author's E-mail address: nmanwar@ichf.edu.pl; jcarloscolmenares@ichf.edu.pl.*

Keywords: Plasmonic Cu_2SSe, Biomass valorization, CO_2 promoted reactions, Photon-driven process.

Introduction. Plasmon-induced catalysis (PIC) is a rapidly growing research interest with many potentially known strategic applications. Over the last two decades, the PIC has been recognized as a promising approach to many conventional thermo-photo-electro catalytic conversions [1]. However, various strategies have been developed to optimize their high catalytic activity in fine chemical synthesis and the associated plasmonic properties can enhance the selectivity and broad light-matter interactions. Indeed, colloidal semiconductor nanocrystals (NCs) of Cu chalcogenides have a unique size and shape-dependent catalytic performance that emerges due to nano-confined quantum dots. Whereas, the associated defects, band-structure engineering, and alloying influences the structural and optoelectronic properties [2]. Owing to the remarkable advances in copper chalcogenides with different sizes, shapes and tuneable compositions have promoted several PIC applications. The ubiquitous thermo-photo-electro catalytic reaction includes selective oxidation, selective reduction, cross-coupling, and addition reactions [3]. Moreover, Cu chalcogenide NCs have gained tremendous attention due to their high abundance, environmental compatibility, potentially stable crystal structures, and broad range of compositions. Thus, PIC with Cu chalcogenide NCs offers a realistic approach for large-scale synthesis and sustainable applications (CO_2 reduction, and biomass valorization), that can alleviate greenhouse gases [4].

Results and discussion. In the present study, we are exploring the cuprous sulfide-selenide (Cu_2SSe) alloy NCs for PIC applications. Nevertheless, the chemical synthesis route is used to prepare the Cu_2S, Cu_2Se, and Cu_2SSe NCs, where the cation exchange mechanism induces the formation of the Cu_2SSe phase. **Fig. (a)** shows the comparative XRD pattern of Cu_2S, Cu_2Se and Cu_2SSe, reveals the structural purity and the phases obtained for Cu_2Se and Cu_2S are significant matches with their JCPDS data (Cu_2Se:65-2982 and $Cu_{1.96}S/Cu_{1.92}S$:29-0578). Indeed, the change in XRD phases of the prepared Cu_2SSe NCs discloses the formation of binary chalcogenide, and these XRD peaks are close matches with JCPDS card number Cu_2SSe:24-0376. **Fig. (b)** and **(c)** show the SEM and AFM images of Cu_2SSe, relate the nanocrystalline nature and exhibit the localized surface plasmon resonance (LSPR) properties. Detailed measurements of LSPR are being persuaded and PIC applications are in progress. Finally, the control experiments are also being performed and will tailor the product selectivity by designing advanced heterostructures with low-dimensional materials.

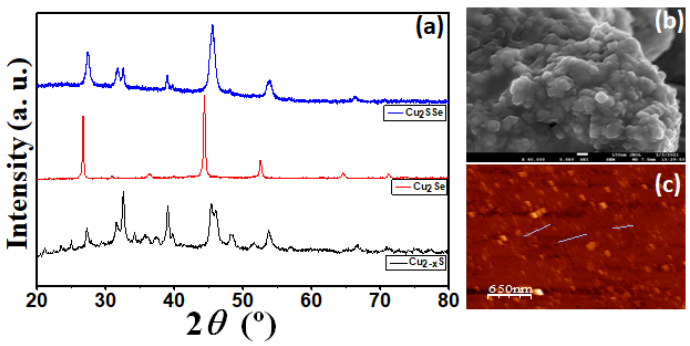

Fig. XRD of Cu_2S, Cu_2Se, and Cu_2SSe (a); SEM of Cu_2SSe (b); AFM of Cu_2SSe (c).

Acknowledgments

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MXenes quantum dots as photocatalysts for hydrogen evolution

Hermenegildo García and Ana Primo*

Instituto Universitario de Tecnología Química, Universitat Politècnica de Valencia-Consejo Superior de Investigaciones Científicas, Av. De los Naranjos s/n, 46022 Valencia, Spain

* *aprimoar@itq.upv.es*

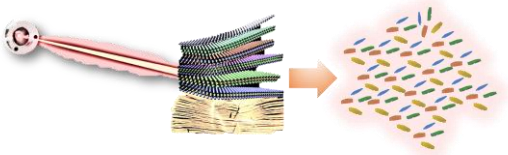
Keywords: Mxenes, photocatalysis, hydrogen

Introduction. MXenes are recently discovered 2D materials that present interesting properties for a wide range of applications. MXenes are constituted by alternate layers of a metal (M) and a carbon or nitride layer (X), the latter always internal and sandwiched between two metal sheets.[1] Normally, these materials are obtained by delamination of the corresponding MAX phase by removal of Al^{3+} with HF.[2] Due to the corrosive and hazard risks associated to the use of concentrated aqueous HF solutions, there is a need to develop alternative green delamination procedures. On the other hand, for application in photocatalysis, it is necessary to control the band gap of these materials and to align the energy of the conduction and valence band to the optimal potentials to promote a particular chemical reaction. Considering the two commented problems of MXene synthesis, it occurred to us that innovative preparation procedures could be used to avoid HF, while transforming a conductive MXene into a semiconductor material for its use in photocatalysis. Herein it is reported that laser ablation of the MAX phases is a general procedure to prepare MXene quantum dots (MxQDs) that are able to evolve hydrogen photocatalytically upon irradiation with Visible light.

Experimental/methodology. *Material preparation*: Preparation of MxQDs was carried out suspending the MAX phase (3 mg) in water (4 mL). The suspension was sonicated and irradiated with the second harmonic of a Q-switched Nd:YAG laser. Formation of MxQDs was followed by measuring periodically the optical absorption and photoluminescence (λ_{ex} 350 nm) of the cuvette.

Photocatalytic experiments: The photocatalytic reactions were carried out using a suspension of the corresponding MxQDs that was re-dispersed in 16 mL of Milli-Q water adding 4 mL of triethanolamine (TEOA) as sacrificial electron donor. The suspension was stirred at room temperature and irradiated with a 300 W Xenon lamp equipped with a cut off filter ($\lambda > 450$ nm) to ensure irradiation with visible light. The evolving gases were analyzed connecting directly the photoreactor to an Agilent 490 Micro GC system.

Results and discussion. Herein, we have reported that 532 nm laser ablation in liquid in the absence of any aggressive reagent produces MXene QDs. The process of MxQDs formation can be conveniently followed by the increase in the optical absorption in the UV and photoluminescence intensity as well as by dynamic laser scattering of the suspension. HR-TEM imaging confirms the crystallinity of the materials and their MXene structure with average lateral particle size of 5 nm, while according to their thickness measured by AFM most of them are constituted by single layer or few layers of MXene QDs. Importantly, the procedure leads to oxygen-terminated MXenes, IR spectroscopy suggesting the presence in some cases of terminal O-H (Ti_3C_2 and Ti_2C QDs) and O (V_2C QDs) groups. The trend in the bandgap energy as a function of the particle size and surface termination of these MxQDs has been estimated by DFT calculations. This strategy should lead to effective band engineering. The bandgap opening in QDs has allowed us to determine the photocatalytic H_2 generation activity in the absence of photosensitizing dyes, giving values in the range of $mmol_{H2}xg^{-1}$ that are in the range of the best photocatalysts, even without further optimization.



Scheme 1. Pictorial representation of the MxQDs preparation procedure by laser ablation

Acknowledgments *Financial support by the Spanish Ministry of Science and Innovation (CEX2021-001230-S grant funded by MCIN/AEI/10.13039/501100011033) is gratefully acknowledged.*

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2D Molybdenum Dichalcogenides by Atomic Layer Deposition towards photo and electrocatalysis

J. Rodriguez-Pereira[1,2*], R. Zazpe[1,2*], J. Charvot[3], L. Hromadko[1,2], H. Sopha[1,2], F. Bures[3], J.M. Macak[1,2*]

[1] *Center of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice, Nam. Cs. Legii 565, 530 02 Pardubice, Czech Republic*

[2] *Central European Institute of Technology, Brno University of Technology, Purkynova 123, 61200 Brno, Czech Republic*

[3] *Institute of Organic Chemistry and Technology, Faculty of Chemical Technology,University of Pardubice, Studentska 573, 53210 Pardubice, Czech Republic*

[*] *jhonatan.rodriguezpereira@upce.cz, raul.zazpe@upce,cz, jan.macak@upce.cz*

Keywords: Atomic Layer Deposition, 2D materials, photocatalysis, electrocatalysis, HER.

Introduction. 2D semiconductor transition metal dichalcogenides have attracted considerable attention due to their layered structure, suitable band gap, electrochemically active unsaturated edges and relatively good stability against photocorrosion. These properties result promising for different applications including, Li-ion batteries, photocatalysis and hydrogen evolution reaction (HER). Apart from the widely studied 2D MoS_2, 2D selenide and telluride equivalents - $MoSe_2$ and $MoTe_2$ - have recently gained considerable interest, due to their higher electrical conductivity, wider inter-layer distance and narrower bandgap (as compared to MoS_2), high surface area and close to zero Gibbs free energy edges for hydrogen adsorption. Unlike sulfide dichalcogenides, the lack of Se and Te precursors have prevented the synthesis of selenide and telluride dichalcogenides by ALD. In order to surpass such impediment, we present a set of novel in-house synthesized Se and Te compounds, which were successfully combined with commercial Mo precursor to synthesize $MoSe_2$ and $MoTe_2$ by ALD [1-5].

Experimental/methodology. The 2D molybdenum dichalcogenides where synthesized by ALD, using commercial precursor for Mo and S, and in-house precursors for Se and Te. The prepared samples where characterized using SEM, TEM, XPS, Raman and XRD. In order to analyze the catalytic performance, photocatalysis (by the degradation of methylene blue and hexane) and electroctalysis (HER in acidic and basic media) tests were performed.

Results and discussion. The as-deposited ALD MoS_2, $MoSe_2$ and $MoTe_2$ on substrates of different nature were extensively characterized by different techniques, which confirmed the chemical composition and revealed the growth of 2D flaky nano-crystalline MoS_2, $MoSe_2$ and $MoTe_2$. In parallel, MoS_2, $MoSe_2$ and $MoTe_2$@TiO_2 nanotube layers (TNTs) heterostructures were fabricated in a simple and fast fashion to explore and exploit the MoS_2, $MoSe_2$ and $MoTe_2$ photo- and electrocatalytic properties. TNTs act as excellent photoactive supporting material providing a high surface area, unique directionality for charge separation, and highly effective charge collection. The presentation will introduce and describe the synthesis of the 2D Mo dichalcogenides, the corresponding physical and electrochemical characterization and encouraging results obtained in HER [4,5], photocatalysis [4-6] and Li-ion batteries [7].

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Pt nanoparticles, clusters and single atom sites on MoS_2 sheets for electrocatalytic water splitting

T. Ollár[1], A. A. Koós[2], P. Vancsó[2], P. Kun[2], P. Nemes-Incze[2], J. S. Pap[1], K. Frey[1] and L. Tapasztó[2]

[1] Surface Chemistry and Catalysis Department, Centre for Energy Research, Hungary
[2] 2D Nanoelectronics Lendület Research Group, Institute of Technical Physics and Materials Science, Centre for Energy Research, Hungary
Corresponding Author's E-mail address: ollar.tamas@ek-cer.hu

Keywords: 2D MoS_2, platinum, nanoparticles, cluster, SACs, HER, electrocatalysis, STM

Introduction:

Transition metal chalcogenides are broadly investigated catalysts, limited by the relative inertness of their pristine basal plane MoS_2 single layers modified by substitutional oxygen can harvest the synergistic benefits of stably anchored single-atom sites and activated MoS_2 basal planes. [1]

MoS_2 single-layer substrates with embedded non-metal heteroatoms also offer the benefit of site densities that are much higher than those reported previously in the literature for metal SACs on various substrates. Substitution of heteroatoms with different electronegativity as compared to the substituted chalcogenide atoms induces a local redistribution of the charge density. This can create a complex charge density landscape where ions can find their preferred sites for efficient adsorption and charge transfer [2].

Experimental/methodology.

The resulting active sites are of interest not only for their catalytic activity but also as anchoring sites for other metal atoms. Taking advantage of this property, we planned to form platinum nanoparticles, clusters and single Pt sites on the surface of 2D MoS_2, and then compared their catalytic properties in electrocatalytic hydrogen evolution reaction.

Results and discussion

The results of the research yielded interesting and forward-looking results from several The ultra-efficient Pt-MoS_2 catalysts are able to reach the activity of commercial Pt-C catalysts at three orders of magnitude lower Pt loadings of ~10 nanograms/cm^2, utilizing Pt a hundred times more efficiently than Pt single atom catalysts.

Acknowledgements

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Ultradispersed Mo sulfide catalysts: single atoms or few-atom clusters?

D. Ryaboshapka[1*], L. Piccolo[1], C. Geantet[1], M. Aouine[1], P. Bargiela[1], V. Briois[2], P. Afanasiev[1]

[1]*Université Claude Bernard Lyon 1, CNRS, IRCELYON, Villeurbanne, France*
[2]*Synchrotron SOLEIL, L'Orme des Merisiers, Gif-sur-Yvette Cedex, France*
[*] *daria.ryaboshapka@ircelyon.univ-lyon1.fr*

Keywords: ultradispersion, molybdenum sulfide, HDS catalysts, operando XAS, hydrogen evolution

Introduction. Layered transition metal (TM) sulfides like MoS_2 (WS_2, ReS_2) are widely studied in reactions involving H_2. The edges of MoS_2 slabs are currently viewed as the active sites. However, along with slabs, small clusters and single atoms (SAs) are present, with unknown structure and activity. Our research is focused on the structure and activity of these subnanometric sulfidic TM entities. Such species might be adsorbed on the support or be embeded into a framework (e.g. of a MOF or of N-doped carbon)[1]. In this work we applied different syntheses to obtain ultradispersed Mo sulfide species, studied their activity in thiophene hydrodesilfurization (HDS) and hydrogen evolution reaction (HER), then followed their evolution during the reactions by XAS *operando*.

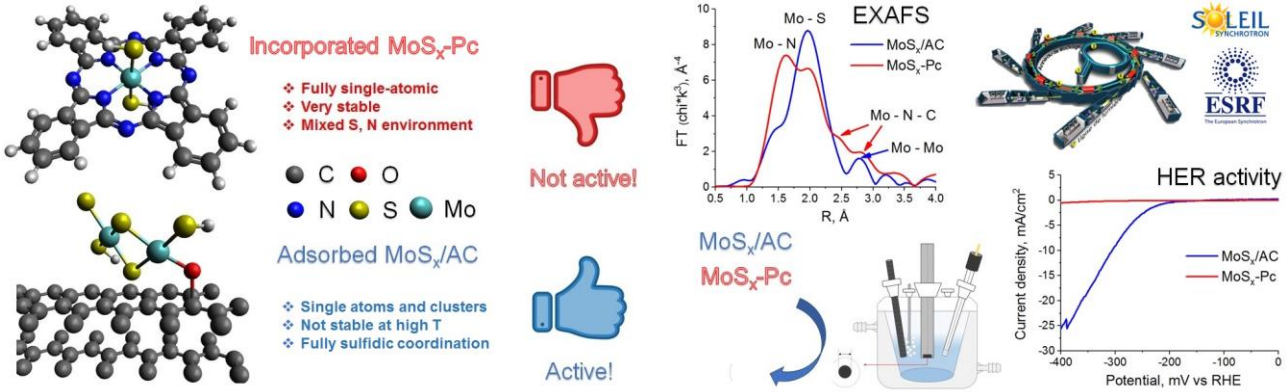

Figure 1 Structures of incorporated and adsorbed MoS_x, the corresponding EXAFS spectra and HER activity

Experimental/methodology. The catalysts (1 wt.% Mo) were obtained via dry impregnation/adsorption or via one-pot routes. Various supports (activated carbon (AC), TiO_2, SiO_2, Al_2O_3) and various one-pot techniques were used. The systems were sulfided in H_2S/H_2 flow and characterized by TEM, UV-vis DRS, Raman, XRD, STEM-ADF and tested in the HDS of thiophene and in the electrochemical HER. The evolution of Mo species during sulfidation and during the HDS and HER reactions was investigated by *operando* QXAS at the ROCK beamline of SOLEIL synchrotron (for HDS) and *operando* HERFD XANES at the FAME-UHD beamline of ESRF synchrotron (for HER).

Results and discussion. The adsorbed few-atom clusters are exemplified by the MoS_x/AC catalyst and incorporated single atoms - by a phthalocyanine polymer MoS_x-Pc (Fig. 1). While MoS_x/AC demonstrated high specific activity per Mo atom in HDS and high current densities in HER, MoS_x-Pc was not active (Fig. 1). Physico-chemical techniques (Raman, STEM..) attest that few-atom clusters and SAs are present in MoS_x/AC,[2] whereas MoS_x-Pc contains only SAs. Operando QXAS has shown that Mo species on AC during sulfidation are transformed into sulfidic oligomers with 2-3 Mo atoms. In the MoS_x-Pc, Mo remains single-atomic, surrounded by 4 N and 2 S atoms (Fig. 1). Both species are stable during the HDS reaction. When exposed to HER conditions in the acidic media the adsorbed MoS_x are oxidized and in MoS_x-Pc sulfur is replaced by oxygen. Our results suggest that both HER and HDS reactions require the presence of several (at least 2) Mo atoms in the active site, whereas fully single-atomic MoS_nN_m species are inactive.

Acknowledgments

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Towards catalyst design and databases for molecular OER catalysis

Michael J. Craig,[1] Cian Clarke,[1] Timo Sommer,[1] Felix Kleuker,[1] Max García-Melchor,[1*]

[1]*School of Chemistry, CRANN and AMBER Research Centres, Trinity College Dublin, College Green, Dublin 2, Ireland*

[*]*E-mail: garciamm@tcd.ie*

Keywords: water oxidation, hydrogen production, catalyst design, machine learning, databases.

Introduction. Despite fossil fuels having brought forth the dawn of civilisation as we know it, they have also left an enduring effect on the Earth's climate. To address this, it is imperative that we devise renewable technologies to decarbonise our economy. For example, one could envision using sunlight to drive (photo)electrochemical water splitting devices to produce H_2, a highly energy-dense fuel when compressed and stored. A major roadblock in realizing this, however, is the lack of affordable and high-performing catalysts for the oxygen evolution reaction (OER).[1]

Experimental/methodology. All the quantum chemical calculations described in this presentation have been performed using density functional theory methods as implemented in the software Gaussian09, while machine learning models have been developed using scikit-learn.

Results and discussion. The first part of this talk will describe our recent findings which demonstrate that molecular catalysts obey the same OER scaling relations observed for heterogeneous systems, and thereby are constrained to the "overpotential wall" imposed by such relations.[2-4] This part will also discuss how some of the most active complexes reported in the literature can circumvent the overpotential wall, and how this knowledge can be translated into a set of catalyst design principles to advance the discovery of "ideal" molecular OER catalysts.

The second part of the presentation will be dedicated to the high-throughput screening of molecular OER catalysts using well-known ligand scaffolds and transition metals, demonstrating the universality and method independent nature of scaling relations.[5] This study has also led to the discovery of new complexes based on earth-abundant elements with predicted activities comparable to Ru-based catalysts, as well as the development of machine learning algorithms to assess OER activity at almost no computational cost and with errors comparable to state-of-the-art DFT methods.[6]

In the final part of this talk, we will outline our ongoing research efforts in the generation of a curated molecular OER database and compliant with the principles of findability, accessibility, interoperability, and reusability (FAIR).

Acknowledgments

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Engineering the Solid State Synthesis and Processing of Nickel Boride Nanocrystals for Electrocatalytic Application

Jennifer Hong,[1,2] Dr. Loredana Protesescu,[1*] Prof. Dr. Paolo Pescarmona[2*]

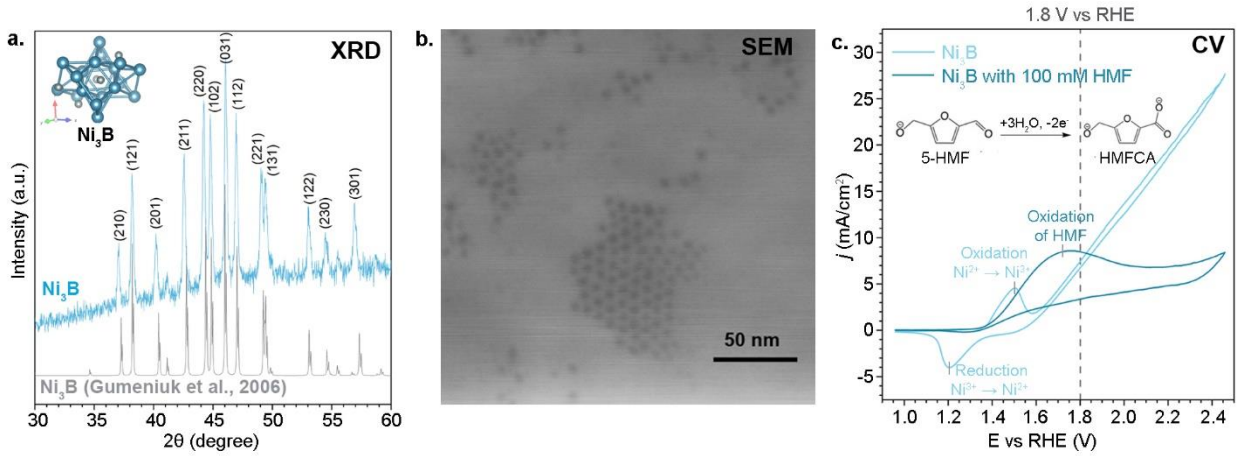
[1]*Material Chemistry, Zernike Institute of Advanced Material (ZIAM), University of Groningen*

[2]*Sustainable Chemical Products and Catalysis, Engineering and Technology institute Groningen (ENTEG), University of Groningen*

Introduction Metal borides (Ni_xB_y, Co_xB_y), a relatively unexplored class of materials, have in recent years started to garner interests as they have shown potential to be efficacious electrocatalysts for water electrolysis under challenging conditions such as high pH or high temperatures.[1] Despite the increased surface area and surface optimization that are commonly displayed by other nanosized materials, the nanostructured M_xB_y remains underdeveloped despite the prospective enhanced performance. The limited development of nano M_xB_y is mainly due to the difficult synthetic process. Recent works have shown that synthetic methods at lower temperatures (<400 ºC) yield amorphous polydisperse nanocrystals (NCs), while phase purity remains an issue at higher temperatures.

Experimental/Methodology Here, a simple, scalable solid-state reaction of metal precursors ($NiCl_2$ or Ni^0, $CoCl_2$) and sodium borohydride ($NaBH_4$) is demonstrated to obtain a phase-pure nanocrystalline Ni_xB_y, Co_xB_y and $(NiCo)_3B$. These nanostructured Ni_xB_y were studied as electrocatalysts for the electrooxidation of the bio-based 5-(hydroxymethyl)furfural (HMF) to produce various useful products. The electrocatalytic tests were performed under the oxidative condition at pH 13 (0.1 M KOH) and constant potential of 1.8 V vs RHE with catalyst loading of 0.05 mg/cm^2.

Results and Discussions Through the solid-state reaction of either metallic Ni^0 or $NiCl_2$ with $NaBH_4$ at a relatively low temperature (400 °C) under atmospheric pressure, crystalline nanosized Ni_2B and Ni_3B could be obtained with high yield in pure phase and with narrow size distribution (15-30 nm) while reaction of $CoCl_2$ and $NaBH_4$ produce exclusively Co_2B NCs. Through extensive mechanistic studies, we show that Ni nanoclusters (*approx.* 1 nm) are intermediate in the boriding process, while the halide precursors lower the decomposition temperature of the $NaBH_4$ (used as a reducing agent and B source). Using reaction mediators, we probe the differential nucleation and growth of Ni (clusters) or Ni_xB_y NCs while using L (amine, phosphine) and X-type (carboxylate) mediators.



The M_xB_y nanopowders obtained was made into solution-processable inks via surface treatment with nafion/DMSO then loaded onto carbon paper support. Compared to the prior study done on the electrooxidation of 5-HMF with Ni_xB_y, we conducted our process at lower pH in order to prevent the formation of humin.[2] Furthermore, we were able to decrease the catalyst loading 20x lower than previously reported while retaining similar activity to samples with higher Ni_xB catalyst loading. Our study reveals the efficiency of Ni_xB NCs in HMF conversion (51%) and the extremely high selectivity towards HMFCA (75%).

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Electrodeposition synthesis of hierarchically structured $LaNi_{0.5}Co_{0.5}O_3$ nanosheets as the cathode of intermediate-temperature Li-O_2 battery

Qianyuan Qiu, Jiaqi Wang, Penghui Yao, Yongdan Li*

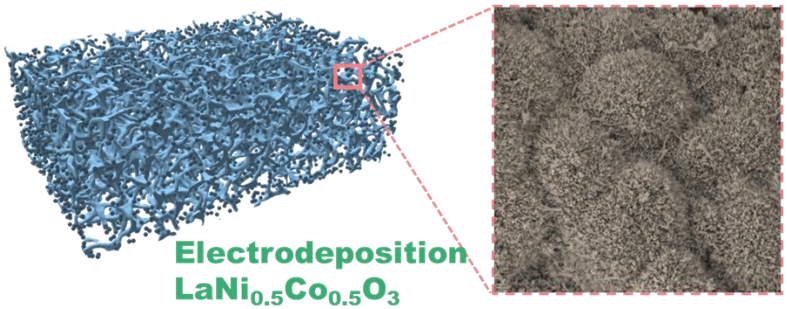
Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Espoo, Finland

Keywords: Electrodeposition, $LaNi_{0.5}Co_{0.5}O_3$, Li-O_2 battery

Introduction. Lithium-oxygen (Li-O_2) batteries with high theoretical energy densities have great potential for a new generation of energy storage technology[1-3]. Their main limitations, however, are the slow kinetics of ORR and OER, the low mass-energy density, and inferior cycling stability compared with other energy storage devices[4]. Our previous work has shown that $LaNi_{0.5}Co_{0.5}O_3$ (LNCO) is a promising candidate for a high-performance cathode catalyst in an intermediate-temperature Li-O_2 battery due to its excellent conductivity and intrinsic catalytic activity. Many techniques, such as sol-gel, template, co-precipitation, and spray pyrolysis, have been developed to synthesize LNCO. However, these methods mostly require high pressure, high temperature, and a long experimental period. Therefore, one of the current challenges is to controllably fabricate large-scale, superior-quality perovskite layers for enhanced efficiency Li-O_2 batteries via low-cost manufacturing processes. Electrodeposition processes have been employed to synthesize nanostructures because of their mild reaction conditions, controllable parameters, and cost-effectiveness. Nevertheless, research on the preparation of LNCO by electrodeposition is not mentioned.

Experimental/methodology. The treated Ni foam working electrode is immersed into a 30 mL solution containing 0.01 M $La(NO_3)_2$, 0.005 M $Ni(NO_3)_2$, and 0.005 M $Co(NO_3)_2$. An Ag/AgCl is used as the reference electrode, and a Pt plate is used as the counter electrode. After 15 cyclic voltammetry measurement between -0.3 V and −1 V (vs. Ag/AgCl) at a scan rate of 5 mV s^{-1} at 70 °C, porous nanosheets $LaNi_{0.5}Co_{0.5}O_3$ is uniformly generated. The obtained product is washed with deionized water for several times and dried at 40 °C in vacuum.

Results and discussion. Here, we present a method for preparing hierarchically structured $LaNi_{0.5}Co_{0.5}O_3$ nanosheets by electrodeposition to develop an intermediate-temperature Li-O_2 battery. In this work, we focus on adjusting electrodeposition parameters, such as temperature, electrolyte concentration, electrodeposition method, time, and solvent, in designing and fabricating LNCO nanosheets. The LNCO nanosheets make the Li-O_2 battery with a high mass-energy density and a long cycle life. The exceptional characteristics of LNCO nanosheets in Li-O_2 batteries at intermediate temperatures make them a potential material for application in metal-air batteries.



Acknowledgments

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Supramolecular organocatalysis with novel BTA helical structure

Dr. Antonio Valverde-González, Prof. Laurent Bouteiller and Dr. Matthieu Raynal
Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, Equipe Chimie des Polymères, 4 Place Jussieu, 75005 Paris, France.

Keywords: enantioselectivity, supramolecular organocatalysis, helix, BTA

Introduction.
Novel catalytic approaches, which possess recognition sites and a modular backbone, may constitute a suitable approach to achieve site selectivity. Supramolecular helical polymers composed of benzene-1,3,5-tricarboxamide (BTA) units, as a scaffold for asymmetric catalysis[1] have proven to be efficient when the BTA ligand is functionalized with an aryl phosphine (PAr_2) moiety that can promote metal-catalyzed reactions such as the rhodium-catalyzed hydrogenation of dimethyl itaconate,[2] the copper-catalyzed hydrosilylation of acetophenone derivatives,[3,4] and the copper-catalyzed hydroamination (HA) of styrene.[5] This is mainly because the fact that BTA monomers assemble in solution through a combination of aromatic and hydrogen bonding yielding well-defined supramolecular helices.[6] The configuration of the product and the selectivity of the reaction are correlated to the handedness and optical purity of the helices, which can be finely controlled by means of stereogenic groups located in the side chain of the BTA ligand[19] or in a phosphine-free monomer (the latter is also called a "sergeant"). However, organocatalytic active species have not been yet incorporated into these helical systems. Specifically, we are interested in hydrogen-bond-donor groups (HBD) such as thioureas with the aim of serve as a direct the interactions with carbonyl containing substrates.

Experimental/methodology.
Benzene-1,3,5-tricarboxamide (BTA) have been prepared with a C_2-symmetry**.** Thus, two long chiral alkyl changed were introduce through and amide formation, whereas in the third position the catalytically active HBD species (with the thiourea moiety) were introduced also through an amide function. Corresponding assemblies were prepared in non-polar solvents (such as toluene) and the corresponding characterizations techniques were applied to confirm both the helicity and formation of the assembly (such as: UV-Vis, CD, FT-IR, NMR and SANS/SAXS). Enantiomeric excess of the catalytic tests was analyzed by HPLC

Results and discussion.
Mixtures of BTA monomers were evaluated in model asymmetric reactions. Analytical data, in combination with control experiments, validate the expected design, i.e. that both thiourea and catalytic moieties act cooperatively for the activation of the substrate.

Acknowledgments
French ANR funding : project "AdECat" ANR-21-CE07-0037-01

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Synthetic considerations of functionalized cyclic and bicyclic (alkyl)(amino)carbenes

M. Nagyházi,[1,2*] V. Farkas,[1,2,3] B. Almási,[1,2] Á. Erdélyi,[1,2] K. Varga,[1,2] Á. Lukács,[1] R. Tuba[1,3]

[1]*Institute of Materials and Environmental Chemistry, Eötvös Loránd Research Network, Research Centre for Natural Sciences P.O. Box 286. Hungary*
[2]*Budapest University of Technology and Economics, Faculty of Chemical Technology and Biotechnology, Műegyetem rkp. 3., Budapest, 1111, Hungary*
[3]*Yale Center for Green Chemistry and Engineering, Yale University New Haven, Connecticut, 06511, USA*
nagyhazi.marton@ttk.hu

Keywords: carbene ligands, organic synthesis, CAAC, BICAAC

Introduction. Ligand development is a useful tool to fine-tune transition-metal complex-based catalyst systems. Hypovalent carbon compounds, carbenes have also emerged as a possible ligand class. As novel molecular skeletons have been discovered, carbenes turned into a widely investigated topic. Modifications on their structures is qiute common in the case of NHC ligands, but still not widely spread at better sigma donor and pi acceptor types, cyclic and bicyclic (alkyl)(amino)carbenes (CAAC and BICAAC). The presentation points out the substitution possibilities of these classes and discusses its impact on their catalytic performance.

Results and discussion. The convenient CAAC and BICAAC ligand syntheses were modified to enable the tuning of the steric and electronic properties of the desired ligands. The substitution on the *N*-moiety enabled steric modifications that had serious impact on the catalytic metathesis of olefins with BICAAC-Ru-alkylidene complexes.[1] On the other hand, the tuning of the alkyl substituent in the vinicity of the carbene atom had impact on the Pd-BICAAC-PEPPSI complex-catalyzed Heck-reaction.[2] Moreover, the polarity of the carbene ligands could also be tuned by applying polar trimethylammonium groups at the *N*-substituent. This modification allowed the preparation of such Ru-alkylidene–CAAC complexes those could convert olefins in polar, protic media like alcolhols, which considered as green solvents.[3] The presentation also gives an overview about the further possible modifications on these ligand systems – illustrated with yet unpublished results.

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Design of organometallic complexes as precursors for catalysts with tuneable properties

L. Frederiksen[1*], P. J. Dyson[1]

[1]*École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland*
[*]*lindsey.frederiksen@epfl.ch*

Keywords: ruthenium, nickel, core-shell, nanoparticles, hydrogenolysis, lignin

Introduction. Coreshell nanoparticles (CSNPs) show excellent stability and selectivity for catalysis due to the presence of a protective shell encapsulating the active nanoparticle surface.[1] The increased stability and selectivity have proven beneficial for biomass conversion to value-added chemicals[2] – an important topic for a more sustainable future. However, there are major challenges with reproducibility and control over nanoparticle properties, particularly in the field of heterogeneous catalysis.[3] Herein we propose a strategy for the reproducible synthesis of nanoparticles with variable properties to help bridge the gap between catalyst preparation and catalyst properties. CSNPs were synthesized from organometallic precusors and applied to C–O bond hydrogenolysis in lignin model compounds under mild conditions (100 °C and 20 bar H_2). By correlating the nature of the organometallic precursors and CSNP preparation method parameters with the structure of the resulting CSNPs, we are developing a methodology for preparing CSNPs with tuneable physical properties. Studying the relationship between CSNP physical and chemical properties allows us to identify key features that indicate greater stability and higher activity in C-O bond hydrogenolysis.

Experimental/methodology. A variety of ruthenium and nickel complexes featuring *N*-heterocyclic carbene (NHC) ligands (Ru-NHC and Ni-NHC) were prepared and used to generate NPs. The NPs were characterized by HR-TEM, XPS, and ICP-OES, and applied to the mild hydrogenolysis (100 °C and 20 bar H_2) of lignin model compounds (diphenyl ether, benzylphenyl ether, and phenethyl phenyl ether) to determine their activity, selectivity, and stability.

Results and discussion. NHC ligands featuring alkyl side chains (Fig. 1) were chosen to emulate the carbon chains of many surfactants previously used to generate stabilized NPs.[4] The length of the carbon chain was varied to study the effect on shell thickness and porosity, and, as a result, the activity, selectivity, and stability of the NPs. After a sequential chemical reduction and pyrolysis of the organometallic precusors, the physical properties, such as shell thickness, can be related to the precursor nature and variables in the NP synthesis method. After application to the hydrogenolysis of lignin model compounds under mild conditions, structure-activity relationships identify the most important physical properties for predicting catalytic activity, stability, and selectivity.

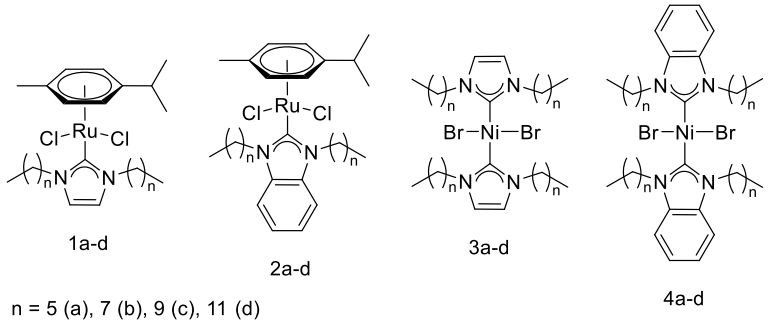

Figure 1. Ru-NHC and Ni-NHC organometallic precursors for the generation of CSNPs.

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Tunable materials with catalytic properties dedicated for chemical and biochemical processes

A. Chrobok[1*]

[1]*Silesian University of Technology, Gliwice, Poland*
[*]*anna.chrobok@polsl.pl*

In this contribution, research on the development of new, specialized catalysts required for designing of clean, environmentally friendly technologies dedicated for the production of high-added value organic compounds for chemical industry will be presented. Heterogenization of the catalyst is one of the most widely favoured green approaches to environmentally friendly process. This goal is achieved by designing of catalysts based on innovative nanomaterials and ionic liquids. The resulting hybrid materials, based on multiwalled carbon nanotubes (MWCNTs) with unique mechanical, magnetic, thermal and electronic properties, as well as non-volatile ionic liquids as "green" media, combine the unique properties of both materials. Ionic liquid can be immobilized on the surface of solid currier *via* chemical bound or *via* physical interactions. Novel ionic liquids with acidic properties, both Brønsted and Lewis acids, will be presented. [1] In addition, ionic liquids based on renewable raw materials, mainly D-glucose, will be presented, which are a convenient environment for enzymatic reactions (Fig.1).[2] The developed catalytic materials are characterized by high activity, selectivity and stability in selected chemical processes: esterification, alkylation, oxidation, cycloaddition, including biomass valorisation and others. Special emphasis will be placed on the improving of biocatalysts activity, selectivity as well as stability in the organic environments. [3-4]

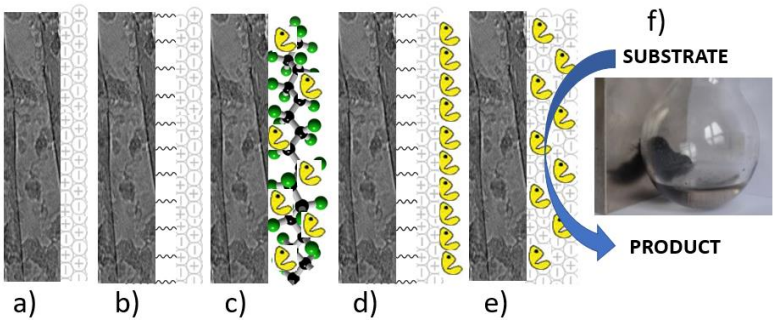

Fig. 1. Tuning of MWCNTs-based catalysts: (a) non-covalent bounding of acidic ionic liquid; (b) covalent bounding of acidic ionic liquid; (c) non-covalent bounding of enzyme to MWCNTs modified with teflon; (d) covalent bounding of ionic liquid to MWCNTs with non-covalent bounding of enzyme; (e) non-covalent bounding of enzyme to MWCNTs modified with ionic liquids; (f) magnetic separation of biocatalyst.

Easy separation of the catalyst from the post-reaction mixture, the possibility of reuse of isolated catalyst to the new reaction cycles and economic availability make the developed technologies attractive for industrial applications. An important issue will also be the presentation of exemplary processes in continuous flow conditions, where separation of the catalyst from the reaction mixture is not necessary, which positively affects the reduction of the number of unit operations, the economy of the process and thus protects the environment.
In summary, ionic liquid-based strategies will be presented as a generic approach to tailoring catalysts for industrially-relevant reactions, to generate both environmentally and economically sustainable processes.

Acknowledgments
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From Theory to Experiments and to Application

M. P. Checinski[1*], K. Stier[1]

[1]*CreativeQuantum GmbH, Berlin, Germany*
[*]*marek.checinski@creative-quantum.eu*

Keywords: Catalysis, Industry, Quantum Chemistry, Mechanism Analysis, Screenings

Introduction
In recent years, computer simulations and especially quantum chemical DFT simulations have become an increasingly important tool to support and accelerate chemical research. Selected examples from academic and industrial research collaborations will be presented to show how useful the combination of experimental and simulations is today.
With the help of simulations, we were able to correct previously proposed popular mechanisms in the chemical literature, and we succeeded in bringing new materials and reactions from the idea via simulations and selected experiments to the application level. On selected examples we are presenting this successful approach.

Experimental/methodology
Mechanism Analysis, Virtual Screening, Selected Experiments, Scaleup

Results and discussion
Organocatalysis: Proline-Catalyzed Cascade Reactions with Carbohydrates

Through an in-depth analysis, we succeeded in developing a suitable mechanism that describes the experimental data of the yields for the proline catalyzed reaction of different carbohydrates with methyl ketones. Here we were able to show that, contrary to the established Houk-List mechanism, the carbohydrate with proline must also be present in order to match the experimental results of our academic partner. Here we were able to show that, contrary to the established Houk-List mechanism, the carbohydrate must also react with proline in order to match the experimental results. [1]

Industrial Catalysis: Ru-Catalyzed Asymmetric Hydrogenation of β-Ketoesters

In this case, we were able to find the most plausible mechanism for this catalytic reaction by investigating many possible individual reaction steps. Here, the focus was on describing the surprising reversal of enantioselectivity at different HCl concentrations. Again, our mechanism deviates from the mechanism known from literature (proposed by Noyori), but describes the experimental results very well. [2]

Methanol Catalysis: Low-Temperature Hydrogenation of Carbon Monoxide

In a very short time, we were able to develop a completely new process for methanol production, from paper to simulations to experimental proof. This process requires significantly less pressure and temperature (120-150 °C, 30-50 bar) than established industrial approaches. This approach is currently being further developed in the project E4MeWi, MeFuSION and scaled-up by the Startup C1 Green Chemicals AG. [3]

Acknowledgments
The authors are also thankful for support for the projects E4MeWi 03El3035A+B, MeFuSION 16RK14003A by the Bundesministerium für Wirtschaft und Energie.

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Exploration of the chemical space: Bridging experimental and computational tools as pathway towards machine learning application for catalyst design

O. Osterthun, J. Henkel, P. Resch, and J. Klankermayer*

RWTH Aachen University, Chair of Translational Molecular Catalysis, Aachen, Germany
osterthun@itmc.rwth-aachen.de and jklankermayer@itmc.rwth-aachen.de

Keywords: homogenous catalysis, machine learning, hydrogenation

Introduction. Modern computational methods, especially with regard to machine learning, are of increasing interest in molecular catalysis. However, application for homogeneous transition-metal catalysts has remained sparse, mainly due to the lack of large high-quality datasets.[1] Recently, we introduced novel derivatives of the triphos ligand (1,1,1-tris(diphenylphosphinomethyl)ethane) and reported their unprecedented activity in Ru-catalyzed hydrogenation reactions.[2] We now set about further optimizing the structure of the triphos ligand and breaking the symmetry of the ligand by modifying a single phosphine arm (Figure 1). This allows fine control over the *trans*-effect and thus, enables specific catalyst tailoring to given substrates. However, since these new triphos^{AB2} ligands result in an increased chemical space of different substitution patterns, classical experimental catalyst synthesis and subsequent catalyst screening becomes unfeasible.

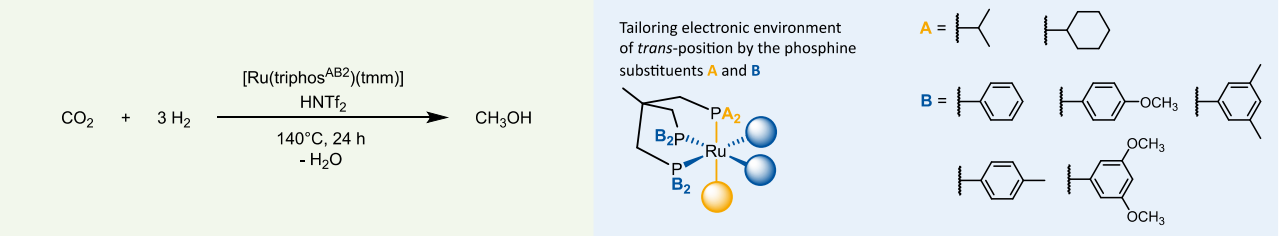

Figure 1: Different [Ru(triphos^{AB2})(tmm)] catalyst structutes investigated experimentally and computationally for the hydrogenation of CO_2.

Experimental/methodology. To understand the mechanistic implications of significantly changing the electronic and steric nature of one coordination site, we use computational methods to describe and investigate the mechanism of [Ru(triphos^{AB2})(tmm)] catalysts in the hydrogenation of carbon dioxide (CO_2). Additionally, the resulting energy spans can subsequently be correlated with the experimental results, which are generated in parallel for selected [Ru(triphos^{AB2})(tmm)] complexes (Figure 1). Further, correlation between molecular descriptors and thermodynamic and kinetic properties are investigated, paving the way for application of machine learning models.

Results and discussion. The application of modern computational methods for mechanistic investigation on the [Ru(triphos^{AB2})(tmm)] catalyzed CO_2 hydrogenation allows us to narrow the chemical space that needs to be probed experimentally. In particular, the incorporation of deactivation pathways into our mechanistic model allows for the first time a qualitative agreement of the computational results with experimental work for the [Ru(triphos^{AB2})(tmm)] catalyzed CO_2 hydrogenation. Furthermore, a careful selection of molecular descriptors allows for a drastic reduction in the computational effort for a qualitative estimation of catalyst performance.

Acknowledgments

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Carbon Nanofiber Supported Mixed Mo and W Carbides for Deoxygenation of Lipid-based Feedstocks

M. Führer, T. van Haasterecht, J.H. Bitter*

Wageningen University, Biobased Chemistry and Technology, Wageningen, The Netherlands
Harry.Bitter@wur.nl

Keywords: mixed metal carbides, carbon nanofibers, characterization, biomass conversion

Introduction

Mono metallic tungsten and molybdenum carbides have been shown to be viable replacements for noble metal catalysts in deoxygenation of biobased feedstocks.[1,2] Though both metals show activity for the deoxygenation of stearic acid, a model compound for biobased lipids, Mo-carbides showed the highest activity. Interestingly, the selectivity is different for carbon supported Mo-carbides to W-carbides catalysts, the former ones are more selective towards oxygenates at low conversion levels, while the W-carbides are more selective towards alkenes at low and high conversions levels.[2] To investigate to which extend we can combine the advantages of both single carbides, we report here on preparation, characterization and performance of carbon nanofiber supported mixed Mo/W-carbides. We will show that the mixed carbides with a higher Mo/W ratio (3:1) reached higher yields of aldehydes and alcohols, while the carbides with a lower Mo/W (1:3) ratio yielded high concentrations of alkenes.

Experimental/methodology

Carbon nanofibers were in house prepared by decomposition at 550 °C of CO/H_2 using a Ni/SiO_2 catalyst. The catalysts were prepared by incipient wetness impregnation with solution of ammonium heptamolybdate and/or ammonium metatungstate to yield catalysts with 0.9 mmol metal $g^{-1}_{catalyst}$ and Mo:W ratios of 3:1, 1:1 and 1:3. The carburization was performed using the carbothermal reduction method. The prepared samples were thoroughly characterized by TEM/EDX, nitrogen physisorption, chemisorption of H_2 and CO, XRD and temperature programmed desorption of ammonia.
The catalysts were tested (without exposing to air) in a batch autoclave for stearic acid deoxygenation in 30 bar H_2 at 350 °C. The turnover frequency (TOF) values were based on CO and H_2 chemisoprtion after 1 hour of reaction.

Results and Discussion

Figure 1 shows a typical TEM/EDX image of the used mixed carbide catalyst and the assesment of TOF as function of Mo loading. The Mo/W ratio was found (not shown in the figure) to influence the product yield towards either oxygenates or alkenes following a hydrodeoxygenation pathway. The more Mo-rich samples have a higher yield towards oxygenates, while the more W-rich samples have higher yields towards the alkene intermediate. The linear relation of the H_2 site based activity together with the evolution of the product distribution as function of the Mo content of the catalyst, suggests that the H_2 site density is a better descriptor for site base activity than the CO site density.

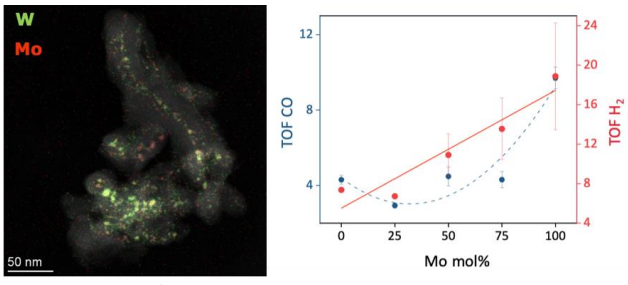

Figure 1: TEM/EDX and TOF of mixed metal carbides

Acknowledgments
Dutch Science Foundation (NWO) for financial support, P. de Jongh and E. de Boed (Utrecht University) for TEM/EDX.

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What are the active sites on Ni/CeO_2 for CO_2 methanation?

S. Tada[1], R. Kikuchi[1*]

[1]*Hokkaido University, Sapporo, Japan*
[*]*rkikuchi8@eng.hokudai.ac.jp*

Keywords: Carbon dioxide, Nickel, Ceria

Introduction. The rapid increase in CO_2 emissions since the Industrial Revolution has made addressing climate change imperative. CO_2 methanation through metal catalysts is crucial for carbon neutrality. Despite high activity reported for Ni/CeO_2 in previous studies [1-3], understanding of the active site structure is limited. This study aims to deepen knowledge on Ni/CeO_2 active sites for CO_2 methanation and provide better catalyst design guidelines, with a focus on investigating the impact of oxygen vacancies on reaction activity.

Experimental/methodology. We made Ni/CeO_2 catalysts using a wet impregnation method, where CeO_2 (JRC-CEO-2 from Catalysis Society of Japan) was impregnated with an aqueous solution of Ni nitrate. The resulting powder was dried at 100°C and calcined at 600°C for 3 hours. Characterization was performed using N_2 adsorption, XRD, H_2-TPR, XPS, and HAADF-STEM. Performance was evaluated in a 4 mm I.D. fixed-bed quartz reactor under atmospheric pressure. 300 mg of catalyst was reduced at 600°C with 5% H_2/Ar before testing. The reactant ($CO_2/H_2/N_2$ = 1/3/1) was fed into the reactor at a GHSV of 10,000 h^{-1}, and the outlet gas composition was monitored using an online micro gas chromatograph (Varian CP-4900).

Results and discussion. We tested CO_2 methanation on Ni/CeO_2 catalysts (Figure 1a). CO_2 conversion increased from 3% to 58% as temperature rose from 250°C to 400°C with 1wt% Ni/CeO_2 catalyst. Above 400°C, CO_2 conversion stayed around 60%. With other catalysts, CO_2 conversion significantly increased as temperature rose from 250°C to 400°C, then reached equilibrium. We also tested CO methanation (not shown). Only 1wt% Ni/CeO_2 had low CO methanation activity.

Based on our performance tests and characterizations, we proposed a CO_2 methanation mechanism for Ni/CeO_2 (Figure 1b). Low Ni loading creates Ni-Ce mixed oxides with Ni-V_{OX}-Ce sites that are active in forming CO through reverse water gas shift. High Ni loading (5 and 10 wt%) results in many metallic Ni nanoparticles supported on Ni-Ce mixed oxides, which are capable of methanating CO.

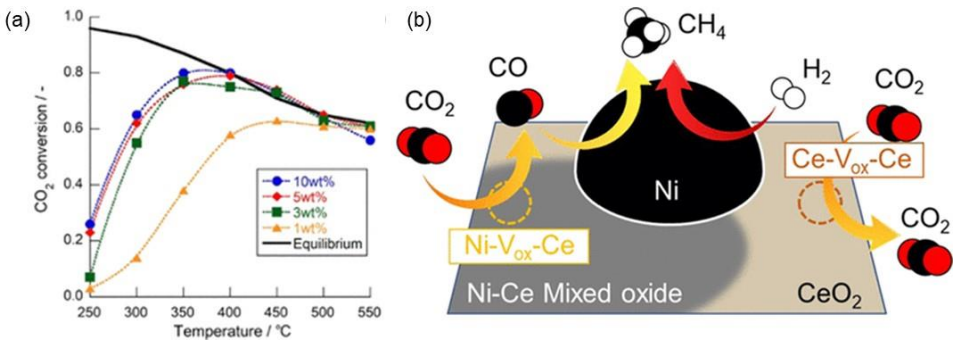

Figure 1 Effect of Ni loading on CO_2 methanation over Ni/CeO_2: (a) CO_2 conversion and (b) CH_4 selectivity. (c) Reaction Mechanism of CO_2 Methanation over Ni/CeO_2. Adapted with permission from [4]. Copyright 2021 American Chemical Society.

Acknowledgments
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Modification of Rh/TiO_2 Single Atom Catalysts with Amine-Fuctionalized Organic Monolayers to Promote CO_2 Hydrogenation

A.H. Jenkins[1], J.W. Medlin[1*]
[1]*Dept. of Chemical & Biological Engineering, University of Colorado, Boulder, CO, USA*
[*]*medlin@colorado.edu*

Keywords: Single atom catalysts, CO_2 reduction, catalyst stability.

Introduction. Significant attention has recently been focused on atomically dispersed supported metals, also referred to as single atom catalysts (SACs), though maintaining stability at elevated temperatures is a challenge. Recently, phosphonic acid (PA) monolayers have been applied to supported metal catalysts[1] and SACs in order to improve catalyst stability and alter adsorbate binding. Modification of Rh_1/Al_2O_3 and Rh_1/TiO_2 SACs with methylphosphonic acid (MPA) improved the sintering resistance of these catalysts without appreciably changing the reaction rate of 1-hexene hydrogenation.[2] In addition, Zakem et al. demonstrated that the deposition of octylphosphonic acid on Rh_1/Al_2O_3 SACs modified the desorption entropy of CO by restricting the movement of $Rh_1(CO)_2$ species.[3] These studies focused on the steric, geometric, and electronic effects PA monolayers have on SACs. Relatively unexplored, however, is the addition of functionalized ligands to SACs in order to introduce additional functionality near the Rh active site.[4] The primary goals of this work were to investigate whether functionalized PA monolayers could enhance reverse water gas shift (RWGS) activity on Rh_1/TiO_2 SACs, to determine the effects of ligand length and functionality on catalytic activity, and to study the effects of PAs on on-stream catalyst stability.

Experimental/methodology. Atomically dispersed Rh on anatase TiO_2 was synthesized using strong electrostatic adsorption at a weight loading of 0.1-0.3 wt%. Various PA SAMs with and without amine groups were deposited to control the position of amine functionality with respect to the single-atom site. Catalysts were characterized with infrared spectroscopy after CO adsorption to confirm atomic dispersion, and a sequential H_2/D_2 scrambling technique was employed to estimate the number of active sites. Adsorption of CO_2 was monitored with infrared spectroscopy both ex situ and under reaction conditions. Reverse water gas shift activity was measured in a differential flow reactor across a range of temperatures.

Results and discussion. We used a combination of infrared spectroscopy and vapor-phase reaction studies to investigate the effects of amine-functionalized phosphonic acids on CO_2 hydrogenation with Rh_1/TiO_2 catalysts. We found that, depending on their tail length, deposition of amine-functionalized ligands such as aminoethyl PA (AEPA) resulted in overall improvements to CO_2 reduction turnover frequency (Fig. 1) and on-stream stability. Interestingly, the activity improvement was highly sensitive to the position of the amine group relative to the surface-bound phosphonate group. Conversely, deposition of alkyl ligands such as propyl PA (PrPA) resulted in blocked CO_2 adsorption and a complete loss of catalytic activity. A sharp reduction in methanation was also observed for phosphonic acid-modified catalysts. However, ligand deposition resulted in a loss in accessible Rh_1 sites, likely due to blocking by tail groups. Our results inform future investigations of ligand-modified single atom catalysts, particularly in terms of achieving ideal metal-ligand proximity.

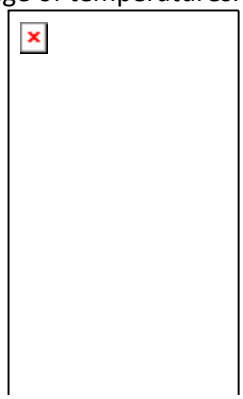

Fig. 1: Turnover frequencies for CO_2 reduction to CO (green) and methanation to CH_4 (red)

Acknowledgments
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Ni-based solid solution catalysts for CO_x-free H_2 generation

Baris Alkan[1, 2], Kassiogé Dembele[1, 2], Gregor Koch[2], Clara Marshall[2], Thomas Lunkenbein[2], and Annette Trunschke[2*]

[1] *Max Planck Institute for Chemical Energy Conversion, Stiftstrasse 34 - 36, 45470 Mülheim an der Ruhr, Germany*
[2] *Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*
[*] *trunschke@fhi-berlin.mpg.de*

Introduction. Ammonia decomposition is one of the promising routes for carbon-free and sustainable hydrogen production. Thermal decomposition by catalysis typically requires high temperatures of about 600 °C for complete conversion of NH_3 to the elements [1]. Although supported ruthenium nanoparticles are highly active, the high cost and scarcity of the metal prevent its use on a large scale. Catalysts based on nickel also show high activities for NH_3 decomposition and are an alternative to Ru [2]. In the synthesis of catalysts, we pursue the concept of incorporating the active metals into oxide host structures. The exsolution of the metal under reductive conditions then leads to highly dispersed and stable metal nanoparticles. In the present work, we systematically investigated solid solutions of Ni in MgO.

Experimental/methodology. $Ni_xMg_{1-x}O$ solid solutions (x=0-0.1) were prepared by calcination of mixed hydroxides $Ni_xMg_{1-x}(OH)_2$ with a brucite type structure synthesized by co-preciptation. Physical properties of the fresh catalysts were determined by XRD, Raman, STEM-EDX, and nitrogen adsorption. The exsolution and dispersion of the Ni nanoparticles was investigated by temperature-programmed reduction (TPR) with hydrogen, H_2 chemisorption, and X-ray diffraction. The NH_3 conversion over $Ni_xMg_{1-x}O$ was compared to those of other supported Ni-based materials and the changes occuring during NH_3 decomposition were investigated through a comparative STEM analysis of fresh, reduced and spent catalysts.

Results and discussion. In the entire composition range studied, the $Ni_xMg_{1-x}O$ precursors are phase-pure. However, electron microscopy indicates that the Ni is not homogeneously distributed, but slightly enriched at the rim of the plate-like nanoparticles. Exsolution of Ni occurs at about 570 °C according to TPR and in-situ XRD (Figure 1a) resulting in highly dispersed Ni metal particles with a narrow particle size distribution (4-5 nm). The minor shift in diffraction peak of $Ni_xMg_{1-x}O$ during reduction is due to thermal expansion. NH_3 conversion over the reduced catalysts increases with increasing Ni content (Figure 1b). The space time yield of Ni exsolved from $Ni_xMg_{1-x}O$ is much higher compared to Ni in a NiO/Al_2O_3-based reference catalyst (Figure 1c). The catalysts show no deactivation in a cyclic test (Figure 1b) and no change in the particle size distribution (Figure 1d). Overall, exsolution of Ni through controlled reduction of host solid solutions based on rock-salt structures is a promising method for developing active and stable NH_3 decomposition catalysts.

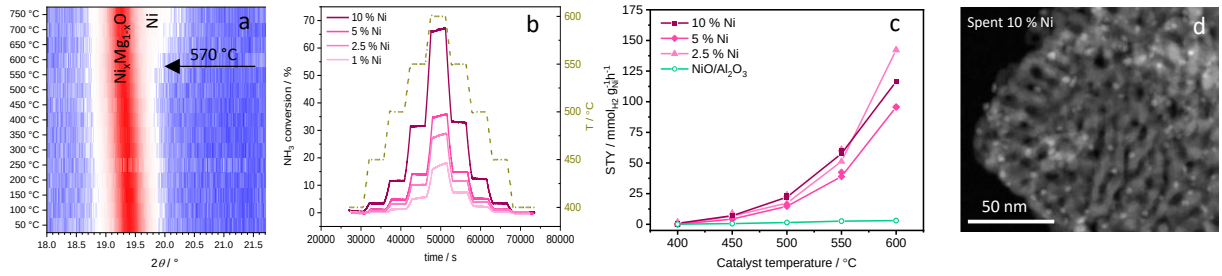

Figure 1 Reduction of 10 % Ni-substituted MgO solid solution recorded by in-situ XRD (a), NH_3 conversion of Ni/NiO-MgO catalysts during heating/cooling cycles at 400-600 °C (feed: 100% NH_3, 600 ml min^{-1} g^{-1}) (b), Space-time yield of H_2 per gram of metallic Ni (c), HAADF image of the spent catalyst showing Ni NPs after NH_3 decomposition (d).

Acknowledgements
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Tuning the catalytic properties of CuZn-based materials synthesized via flame spray pyrolysis and hydrothermal methods for the production of hydrogen from methanol

K.Ar. Papageorgiou[1], A. Zindrou[2], Y. Deligiannakis[2], M. Kuśmierz[3], G. Słowik[3], W. Gac[3] and J. Papavasiliou[1*]

[1]*Department of Materials Science, University of Patras, Patras 26504, Greece*
[2]*Department of Physics, University of Ioannina, Ioannina 45110, Greece*
[3]*Faculty of Chemistry, Maria-Curie Skłodowska University, 3 M. Curie-Skłodowkska Sq., 20-031 Lublin, Poland*
[*]*ipapavas@upatras.gr*

Keywords: hydrogen, methanol, fuel cell, steam reforming, copper catalysts

Introduction. Worldwide strategy plans for decarbonization of energy sector by 2050, are based on hydrogen and renewable sources. In order to avoid technical obstacles regarding the storage and transportation of pure hydrogen, liquid fuels can be employed as hydrogen carriers. Among these fuels, methanol is an attractive fuel, that can be produced from biomass and from green hydrogen and waste carbon dioxide. Hydrogen can be easily produced via steam reforming of methanol (SRM) over commercially available CuZn(Al)O_x catalysts operating between 200 and 300°C with high hydrogen yields and very low CO selectivity [1]. However, these catalysts usually suffer from sintering and pyrophoricity phenomena. In order to avoid possible deactivation, appropriate promotion of the catalytic properties can be done either by tuning the synthesis parameters or/and doping with various metal (oxides). High dispersion and stabilization of the active metallic copper sites and operation at lower temperatures (<200°C) are desired. In addition, the latter characteristic simplifies the integration of a methanol reformer with a high temperature PEM fuel cell. In this work, CuZn-based catalysts were synthesized via Flame Spray Pyrolysis (FSP) [2] and Hydrothermal (HTM) [3] methods. The obtained materials were evaluated in the SRM process and were characterized with various techniques including BET, XRD, XPS, TPR, SEM, HR-TEM, while in-situ DRIFTS were employed to elucidate reaction pathways.

Experimental/methodology. The catalysts were synthesized via: (i) hydrothermal method, at 120-180°C for 24 h, employing metal nitrates (40wt.%CuO, 60wt.% ZnO), and NaOH or Na_2CO_3 as precipitating agents, followed by calcination at 300°C; (ii) Double-Nozzle (DN) FSP, an easily scaled up method able to provide ultrafine CuZn oxide nanocatalysts, doped with various oxides, such as Al_2O_3 or/and Ga_2O_3. The catalysts were tested under SRM conditions within the temperature range of 160-280 ℃ (W_{cat} = 0.3 g, F_T = 70 ccm, S/C ratio = 1.1-1.5, MeOH = 6.5-30%, He as balance). Inlet/outled gas streams were monitored with a GC/MS system. Mapping of the physicochemical properties was done via N_2 adsorption, XRD, XPS, H_2-TPR, SEM and TEM. CO-, MeOH- and H_2O-MeOH in-situ DRIFTS were carried out on selected catalysts.

Results and discussion. Highly active and selective catalysts were obtained via hydrothermal method applied at 120°C with Na_2CO_3 as precipitating agent. These catalysts showed better performance than the corresponding samples prepared via FSP, showing comparable activity and lower CO selctivity with the commercial HiFuelR120. Moreover, remarkable perfomance could be achieved at temperatures as low as 160°C, opening new tecnological prospects in fuel processing integrated with HT PEM fuel cells. In-situ DRIFTS measurements revealed the dissociative adsorption of MeOH towards methoxy and formate species even at relatively low temperatures, while CO_2 and CO became emerged at higher temperatures.

Acknowledgments

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Modification of supported Pt nanoparticles with basic metal oxide clusters for *N*-formylation reaction using CO_2 as a carbon source

Y. Matsunaga[1], S. Kikkawa[1], S. Yamazoe[1,2*]

[1]*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Tokyo, Japan*
[2]*Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, Tokyo, Japan*
[*]*yamazoe@tmu.ac.jp*

Keywords: Supported noble metal catalyst, basic metal oxide cluster, CO_2 fixation reaction

Introduction. The supported metal nanoparticle (NP) catalysts have been used for industrial processes, and their catalytic reactivity has been developed by controlling the size, shape, and surface electronic state of the NPs. We have reported that the modification of basic metal oxide clusters (polyoxometalate, POM)consisting of Nb and Ta[1)] on the surface of supported Au NPs, and the design of a high density of POM–metal interface, lead to highly efficient hydrogenation of aromatic nitro compounds[2)]. We also reported that *N*-formylation of various amines including piperidine proceeds under CO_2 and H_2 atmosphere by using Pt-containing Nb oxide cluster $[Pt(Nb_6O_{19})_2]^{12-}$ as a catalyst[3)]. We observed Pt NPs modified with POM are formed during the reaction, so considered the bifunctional catalysis of the basicity of POM, and the redox property of Pt NPs promoted the *N*-formylation reaction. In this study, we designed the supported Pt NPs catalyst modified with basic POM ($[M_6O_{19}]^{8-}$, M = Nb, Ta) and applied them to the *N*-formylation reaction using CO_2 as a carbon source.

Experimental. Supported Pt catalysts (Pt/Al_2O_3) were prepared by an impregnation method. Al_2O_3 was dispersed in an aqueous solution of $Pt[(NH_3)_2(NO_2)_2]$ (equivalent to 5.0wt%), and then evaporated at 80°C. The resulting sample was calcined and reduced with H_2 at 400°C to obtain Al_2O_3-loaded Pt NPs (Pt/Al_2O_3). $[M_6O_{19}]^{8-}$-modified Pt/Al_2O_3 (M = Nb, Ta, M6-Pt/Al_2O_3) was prepared by an adsorption method. Pt/Al_2O_3 was dispersed in $K_8Nb_6O_{19}$ and $K_8Ta_6O_{19}$ aqueous solutions (POM/Pt atom = 4) under N_2 atmosphere, and the following suction filtration and drying. The N-formylation of piperidine was carried out in an autoclave (piperidine: 0.1 mmol, methanol: 2 mL, catalyst: 24.7 mg (Pt; equivalent to 5.0 μmol), CO_2/H_2: 1.0/2.0 MPa, reaction temperature: 130°C, reaction time: 48 h).

Results and discussion. STEM images of Pt/Al_2O_3 showed that Pt NPs were highly dispersed on Al_2O_3 support and the average particle size was 1.5 nm. The aggregation of Pt NPs was not observed both in Nb6-Pt/Al_2O_3 and Ta6-Pt/Al_2O_3. From the Nb K- and Ta L_3- edge XAS of M6-Pt/Al_2O_3, the Fourier transform of the EXAFS spectra indicated that Lindqvist-structure of $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$ are maintained after the modification on the surface of Pt NPs. Figure 1 shows the product yields in the *N*-formylation reaction of piperidine with CO_2 as a carbon source. The yield of 1-formylpiperidine increased by the modification of Pt/Al_2O_3 with $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$. The addition of Cs_2CO_3 (2.1 mg) to Pt/Al_2O_3 also increased the activity, suggesting that the modified basic POM plays an important role in the reaction. In conclusion, we found that the *N*-formylation reaction using CO_2 as a carbon source proceeded efficiently by the cooperation between the reducing ability of the supported Pt NPs and the basicity of the modified POM.

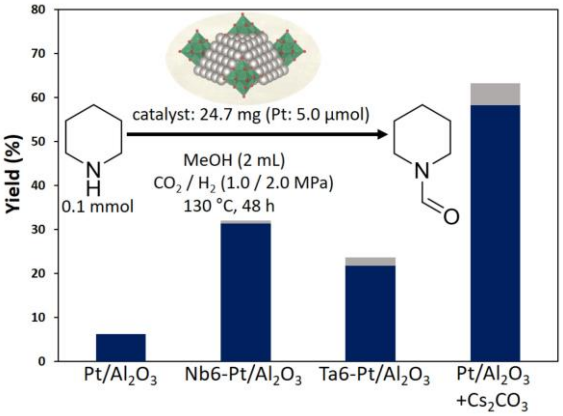

Fig. 1. Product yield of *N*-formylation of piperidine

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Supported Pt and Pt/Ni nanoparticles from metal carbonyl clusters as effective catalysts for biobased molecules valorisation

F. Liuzzi[1,2], C. Cesari[1,2], N. Dimitratos[1,2], S. Zacchini[1,2], S. Albonetti[1,2*]

[1] *Department of Industrial Chemistry "Toso Montanari", University of Bologna, Bologna, Italy*
[2] *Center for Chemical Catalysis "C³", University of Bologna, Bologna, Italy*
[*] *stefania.albonetti@unibo.it*

Keywords: Metal carbonyl clusters, supported metal nanoparticles, biomass valorisation

Introduction. In the last decades, supported metal nanoparticles (NPs) have been widely employed in heterogeneous catalysis to obtain high-performance catalysts. Below 5 nm, chemistry of nanoparticles has lots of similarities with that of metal clusters and high-nuclearity clusters can be considered monodisperse and atomically defined metal nanoparticles. For this reason, metal carbonyl clusters (MCC) can play a role in better understanding and developing of the chemistry of ultrasmall NPs.[1] Particularly, thanks to their chemical and structural composition, MCC have been considered promising precursors for the preparation of metal nanoparticles-based catalysts. [2,3]

The main purpose of this work was to investigate the preparation of several heterogeneous Pt and Pt/Ni-based catalysts with the objective to minimise the use of Pt content, obtained by the effective decomposition of carbonyl cluster over TiO_2. Catalytic performances of the prepared catalysts were evaluated in the 5-hydroxymethyl-furfural (HMF) oxidation using base-free conditions and furfural reductive amination.

Experimental/methodology. A series of random alloy carbonyl clusters $[NBu_4]_2[Pt_{6-x}Ni_x(CO)_{12}]$ with different Pt:Ni molar ratios were synthesised and supported on TiO_2 by wet impregnation, under nitrogen atmosphere.[4] The final catalysts were obtained through a decomposition of the cluster under controlled atmosphere. Each catalyst was tested in the base-free oxidation of HMF, carrying out the reaction in a stainless-steel autoclave, in water under 10 bar of O_2. Some selected catalysts were also evaluated for the reductive amination of furfural, performing the tests in an autoclave, using a NH_3 solution and funder H_2 pressure.

Results and discussion.

IR spectra obtained on cluster modification during each synthetic step highlighted that carbonyl clusters were completely decomposed only after a thermal treatment at high temperature. Moreover, the Pt and Ni distribution, evaluated by TEM analysis, confirms the formation of small and well dispersed Pt NPs, with an average diameter under 2 nm and narrow distributions, while Ni species appear to be dispersed on support surface suggesting the formation of a NiO_x layer. All Pt/Ni cluster-derived catalysts tested in base-free HMF selective oxidation to furandicarboxylic acid (FDCA) exhibited good performances: the presence of a Pt/Ni molar ratio of 5:1 improved HMF conversion up to 90% without the use of a base. This enhancement can be attributed to the formation NiO_x during cluster decomposition. Indeed, its basic properties can improve the catalytic activity. The presence of Ni species also contributes to the catalyst stability, in fact monometallic Pt catalyst presents an activity-loss after two reaction cycles, while bimetallic Ni/Pt materials remain stable for more cycles. The catalytic performances of the samples prepared using carbonyl clusters are significantly improved for both reactions, HMF oxidation and reductive amination of furfural respect to similar systems prepared via incipient wetness impregnation of metallic salts. These results highlighted that cluster decomposition on a support can be a suitable approach to design bifunctional active and stable catalysts promoting the formation of metallic nanoparticles over metallic oxide film.

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Dealumination Effect on the Catalytic Properties of Ni-BEA Zeolite Catalyst in the Dry Reforming of Methane

D. Samoylenko[1*], P. Kyriienko[1], S. Soloviev[1], I. Remezovskyi[1], S. Orlyk[1], S. Dzwigaj[2],

[1]*L.V.Pisarzhevskii Institute of physical chemistry of NAS of Ukraine, Kyiv, Ukriane*
[2]*Laboratoire de Réactivité de Surface Sorbonne Université-CNRS, Paris, France*
[*]*d.samoylenko96@gmail.com*

Keywords: Ni-BEA zeolites, silicate module, Dry Reforming of Methane

Introduction. The dry reforming of methane (DRM) is potentially suitable for industrial conversion of natural gas or biogas into syngas. Zeolites are a perspective group of materials to consider as carriers for catalysts with ability to ensure high dispersion of the active metal on the surface [1]. The disadvantage of zeolite catalysts is their high Brønsted acidity, which stimulates the deposition of coke on the surface of the catalyst under the conditions of the DRM process, and as a result, its deactivation. It was shown previously that Ni-BEA catalysts prepared by the two-stage post-synthesis method show high activity in the production of hydrogen by the partial oxidation of methane. It can be assumed that the stability of the catalyst for DRM at low temperatures can be improved by incorporating nickel into the vacant T-atom sites of the dealuminated zeolite BEA (SiBEA) [2].

Experimental/methodology. Nickel-containing BEA zeolites were prepared by a conventional wet impregnation method and a two-steps postsynthesis procedure, which allow to control the introduction of Ni-ions in the zeolite framework. As a result, a number of BEA zeolite with different degrees of dealumination were obtained, which were marked respectively to their silicate module (Si/Al): NiBEA-17, NiBEA-100, NiBEA-1700. Catalysts were characterized by XRF, SEM, XPS and IR-spectroscopy of adsorbed pyridine. The activity of obtained catalyst samples was tested in temperature range between 500 and 800 °C, the stability test was performed during 8 hours and 700 °C. The ratio of methane to carbon dioxide was 1 to 1, GHSV = 12000 h^{-1}.

Results and discussion. Results of the catalyst activity study shows, that the degree of dealumination is the determining parameter which affects the activity of Ni-BEA catalyst. The most active sample was NiBEA-1700 (Si/Al = 1700). Catalysts based on non-dealuminated zeolite showed weak actity and rapid deactivation during stability test. Instead, NiBEA-1700 retains high activity over several catalytic cycles. In particular, > 50% conversion of methane and CO_2 is achieved already at 700 ºC at high volumetric velocities. In the study of the DRM process, when methane is not purified from sulfur compounds, gradual deactivation of the catalyst is observed as a result of its poisoning. Roasting of zeolite catalyst at temperature of 800 ºC in air allows partial regeneration of the catalyst.

Table 1. Catalytic experiment results

	Ni-BEA-17		Ni-BEA-100		Ni-BEA-1700	
T, ºC	X(CH4),%	X(CO2),%	X(CH4),%	X(CO2),%	X(CH4),%	X(CO2),%
600	4	5	13	25	22	31
700	6	9	26	47	48	58
800	14	17	59	75	79	80
850	20	34	75	84	96	95

Investigation of the acid characteristics of zeolite catalysts with IR-spectroscopy of adsorbed pyridine indicates that with an increase in the level of dealumination, the number of Brønsted acid sites (BAS) and Lewis acid sites (LAS) will decrease. In particular, on the surface of the catalyst with Si/Al = 1700, there is a complete absence of BAS. On the surface of the catalyst there LAS are formed with the participation of aluminum and nickel cations.

Overall, increasing of dealumination degree of Ni-BEA zeolites leads to increasing of their catalytic activity in DRM and resistance to carbonization. The Ni-BEA-1700 sample showed highest activity and stability during several catalytic cycles.

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Encapsulated Ni-CeO_2 nanoparticles with SiO_2 shell for dry reforming of methane

Jae Hyeon Kwon[1], Jong Wook Bae[1*]

[1]*School of Chemical Engineering, Sungkyunkwan University (SKKU), 2066 Seobu-ro, Jangan-gu, Suwon, Gyeonggi-do 16419, Republic of Korea*
[*]finejw@skku.edu

Keywords: Dry reforming of methane (DRM), Ni-CeO_2 nanoparticles, Core-shell catalysts, Ceria promoter

Introduction

Dry reforming of methane with carbon dioxide ($CH_4 + CO_2 = 2H_2 + 2CO$, DRM) have been largely investigated to produce syngas using Ni-based heterogeneous catalysts and product gases can be recycled with subsequent conversions to liquid fuels and chemicals [**1,2**]. Generally, Ni nanoparticles having a comparable activity as novel metals can be easily sintered to form less active and larger aggregates with more facile coke deposition natures for dry reforming of methane [**3,4**]. Cerium oxide can be used to activate CO_2 with its oxygen vacant sites, which enhance the gasification of the adsorbed coke precursors. Moreover, core-shell structure can impart the thermal stability of Ni nanoparticles with spatial confinement effect. In the present study, the strategies for stabilizing the Ni-CeO_2 nanoparticles with less coke depositions are explained by introducing core-shell-structured Ni-Ce@SiO_2 in terms of their resistances for cokes and aggregations.

Experimental

Ni-CeO_2 nanoparticles having different Ce/Ni molar ratios were coated with SiO_2 shells by using the modified reverse microemulsion methods in the Brij C10 / cyclohexane solution (denoted as Ni-Ce_x@SiO_2). Catalytic activity of the reduced Ni-Ce@SiO_2 catalysts were evaluated by using a fixed-bed tubular Inconel reactor with an outer diameter of 9.53 mm. The DRM reaction was carried out with a mixed gas of $CH_4/CO_2/N_2$ (molar ratio) of 1/1/2 at a gas hourly space velocity (SV) = 30,000 mL/(g_{cat}·h), T = 800 °C and P = 0.1 MPa. The effluent gases were analyzed with an on-line gas chromatography (YL6500 GC, Younglin) equipped with a thermal conductivity detector.

Results and discussion.

TEM images of the reduced and used core-shell Ni-Ce@SiO_2 are displayed in **Figure 1(A)**, which clearly showed the uniformly dispersed Ni-CeO_2 nanoparticles were encapsulated with SiO_2 shells. As displayed in **Figure 1(B)**, the conversions of CH_4 and CO_2 on the Ni-Ce_1@SiO_2 (Ce/Ni molar ratio of 1/1) with thermally stable core-shell structures were found to be kept for 250 h on stream. This was also attributed to the highly dispersed Ni nanoparticles during the high temperature DRM reaction.

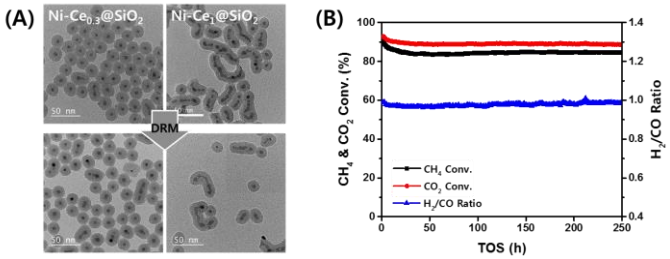

Figure 1. (A) TEM images of reduced and used Ni-Ce@SiO_2 and (B) long-term catalytic stability on the Ni-Ce_1@SiO_2.

The positive contributions of cerium oxides can be enlarged by increasing Ce/Ni ratios on the Ni-Ce@SiO_2 catalyst due to a more abundant supply of lattice oxygen to oxidize the carbonaceous species. The highly dispersed and intimately interacted oxygen vacancies of CeO_2 promoter seems to efficiently suppress the coke depositions as well as structural deformations with the help of the SiO_2 shells.

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Carbon nanofiber growth from methane over carbon-supported NiCu catalysts: Two temperature regimes

S. Schoemaker[1], T. Welling[1], D. Wezendonk[1], B. Reesink[2], A. van Bavel[3], P. de Jongh[1]*

[1] *Materials Chemistry and Catalysis, Universiteit Utrecht, Utrecht, The Netherlands*
[2] *BASF Nederland bv, De Meern, The Netherlands*
[3] *Shell Global Solutions International B.V., Amsterdam, The Netherlands*
Corresponding Author: p.e.dejong@uu.nl

Keywords: carbon nanofibers; growth mechanism; methane; thermogravimetric analysis

Introduction. An attractive route towards CO_2-free production of hydrogen is the thermocatalytic decomposition of methane. Next to hydrogen, valuable carbon nanomaterials can be formed.[1] The carbon nanomaterials have interesting properties, e.g. high electron conductivity and mechanical strength.[2] The properties depend strongly on the carbon structure. To tune the properties, it is key to understand the carbon formation, and how it is influenced by the catalyst properties or reaction conditions.[1,2] Many different kinetic properties or optimal conditions have been reported in literature but there is no detailed conceptional framework yet. In this work, the carbon growth was studied in-situ gravimetrically. We focussed on how the reaction parameters influenced the carbon formation over carbon-supported NiCu catalysts.

Experimental. Ni-Cu catalysts were prepared via incipient wetness impregnation. The decomposition experiments were performed in a thermogravimetric analyzer. The catalysts were reduced *in-situ* after which the sample was heated to reaction temperature and CH_4 gas was introduced. Experiments were performed at varying temperature or with varying methane partial pressure.

Results. We identified two distinct temperature regimes. Operating in the different regimes yielded different kinetic properties (activation energies and reaction orders) and formation of different carbon nanostructures. We offer an explanation by considering a change in the rate limiting step upon operating in different regimes: methane dissociation at lower temperature or carbon formation at higher temperature. A maximum carbon yield was obtained at the transition between the regimes, as here the catalytic system is best balanced. Our results offer understanding of the importance of in which regime one is operating in order to understand how reaction conditions influence the catalytic lifetime and what carbon nanostructures are formed.

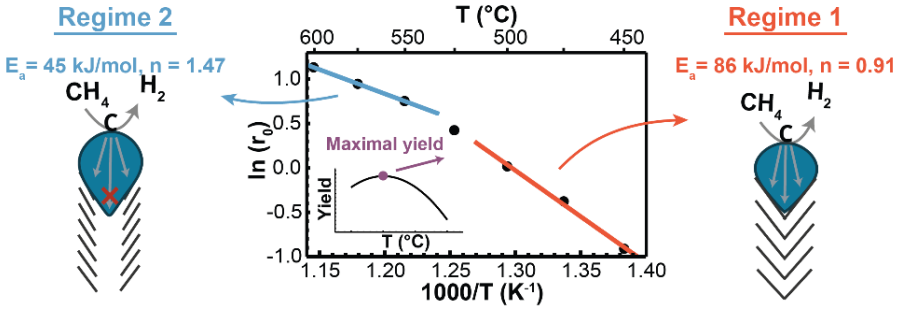

Figure 1 Graphical illustration of carbon growth in two regimes. A maximal carbon yield is obtained at the transition between the regimes.[3]

Acknowledgments

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Developing alumina-based cobalt catalyst for efficient hydrogen production via the ethanol steam reforming process

G. Grzybek[1]*, M. Greluk[2], A. Kierys[2], A. Sienkiewicz[2], J. Lupa[2], G. Słowik[2], M. Rudzińska[1], D. Potyczka[1], P. Stelmachowski[1], A. Kotarba[1]

[1]*Faculty of Chemistry, Gronostajowa 2, 30-387 Krakow, Jagiellonian University, Poland*
[2]*Faculty of Chemistry, Maria Curie-Sklodowska University in Lublin, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland*
[*]*Corresponding Author: g.grzybek@uj.edu.pl*

Keywords: cobalt catalyst, alumina support, alkali doping, ethanol steam reforming, hydrogen production, carbon deposit removal.

Introduction. Production of hydrogen, considered a fuel of the future, is becoming essential in the light of ongoing energy transformation. It can be produced from bioethanol in the catalytic steam reforming process (ESR). A wide range of catalytic systems was investigated in ESR, among others the cobalt phase dispersed over oxide supports [1]. Unfortunately, they suffer from poor stability, mainly due to coke formation upon ethanol dehydration path, which leads to undesired C_2H_4 [2]. This path can be, however, significantly reduced or even eliminated by a controlled modification of the catalyst surface acidity and/or active phase dispersion. In the case of alumina-based systems low acidity may be achieved by using the alpha alumina polymorph [3], while the adjustment can be achieved by alkali doping. Also, the specific surface area of the catalyst is an important factor. To develop an efficient catalyst based on an alumina support, the compromise between its phase composition and internal structure has to be found. In turn, the optimal dispersion of the active phase can be gained by optimizing a method of introduction.

Experimental/methodology. We synthesized a series of cobalt catalysts based on alumina supports varying in phase composition and morphology (different synthesis methods). In addition, we optimized the method of cobalt active phase dispersion over Al_2O_3 and verified the effect of potassium modification. The samples obtained via the incipient wetness impregnation method, sonochemical synthesis, and hydrothermal synthesis were compared. The prepared samples were characterized with a wide range of methods (e.g. XRD, *in situ* XPS, SEM, TEM/EDX, H_2-TPR, RS, TG/DSC) and tested in the ethanol steam reforming process (500°C, EtOH:H_2O 1:12, 21 h). The state of the potassium promoter was studied using a unique thermal alkali desorption method (SR-TAD).

Results and discussion. We compared two series of cobalt catalysts based on Al_2O_3 supports, one pure alpha phase (α-Al_2O_3) and the second containing 79% of alpha and 21% of gamma phase ($\alpha\gamma$-Al_2O_3). The cobalt active phase in the amount of 10 wt% was loaded using three different methods (mentioned above). First of all, using catalysts from both series assured almost no C_2H_4 production (< 1%). The samples based on $\alpha\gamma$-Al_2O_3 show a significant advantage over those containing α-Al_2O_3 in terms of ethanol conversion. Moreover, we observed significantly higher ethanol conversion for catalysts prepared using the sonochemical and hydrothermal method for cobalt dispersion. Adding a potassium promoter allowed for achieving 100% conversion of ethanol. Thus, the adjustment of the alumina support properties (phase composition and internal structure), the method of cobalt introduction, and the loading of potassium promotor allow us to get an efficient ESR catalyst. The observed performance of the catalysts was discussed in terms of the cobalt dispersion, cobalt oxidation state, active phase-support interactions, catalyst surface acidity, and the resistance to deactivation of the catalyst.

Acknowledgments
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Pt single-atom catalyst (SAC) supported on the UiO-66(Ce) for the low-temperature CO oxidation reaction

S. Rojas-Buzo[1,2], B. Bohigues[2], D. Salusso[1], A. Corma[2], M. Moliner[2*], S. Bordiga[1*]

[1]*Department of Chemistry and NIS Centre, University of Turin, Via Giuria 7, 10125 Turin, Italy*

[2]*Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022 València, Spain*

[*]*Corresponding Authors mmoliner@itq.upv.es; silvia.bordiga@unito.it*

Introduction. CeO_2 is a well-defined support in heterogeneous catalysis that can stabilize very disperse metal species under real reaction conditions due to its special electronic properties.[1] In this sense, the analogous subnanometric cerous oxide units presented in a MOF structure can serve also as support of actives metal single sites for many catalytic processes, including, the low-temperature CO oxidation reaction,[2] due to the presence of oxygen vacancies.[3]

Experimental/methodology. The synthesis of the single-atom Pt supported on the UiO-66(Ce) material was carried out by a wet-based impregnation methodology under basic conditions. 150 mg of the as-obtined Pt/UiO-66(Ce) were loaded into a conventional tubular plug-flow reactor for the catalytic test.

Results and discussion. We have made a post-synthetic Pt-MOF functionalization based on an efficient electrostatic deposition. The hydroxyl groups present on the CeO_x clusters after the missing-linker process, can be deprotonated under basic conditions and consequently interact with the cationic Pt species (see scheme in Figure 1). In this sense, and thanks to the combination of different techniques, we claimed the success incorporation of Pt-single sites. Ce L_3-edge XANES and FTIR spectroscopies indicate a consumption of Ce^{4+} species and consequently an increment of Ce^{3+} after the Pt deposition. Moreover, Pt L_3-edge XANES and CO-FTIR spectroscopies confirm the cationic nature of the supported $Pt^{\delta+}$ ($2+<\delta<4+$) on the Ce-MOF. The co-existence of Ce^{3+} sites, able to activate oxygen molecules, and $Pt^{\delta+}$, that can activate the CO molecules, suggested us the possibility to apply this material on the catalytic CO oxidation reaction.

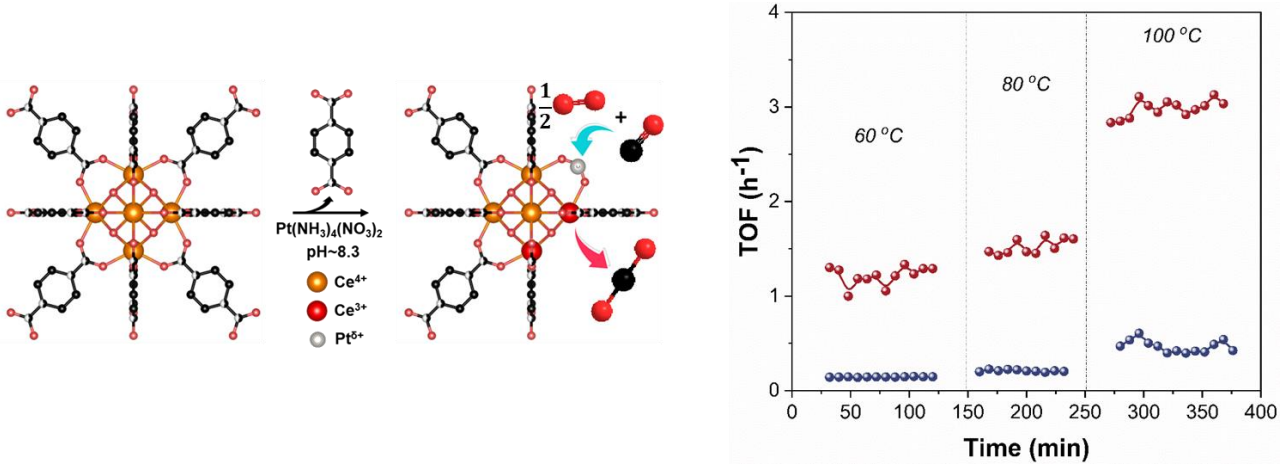

Figure 1. Temperature-programmed CO oxidation obtained for Pt/UiO-66(Ce) (red circles) and Pt/*n*CeO_2 materials (blue circles).

In fact, the Pt/UiO-66(Ce) synthesized in this work shows an increment of ~6-fold in comparison with the traditional Pt/*n*CeO_2 material in the low-temperature range (60-100ºC) studied (see Figure 1). Moreover, its catalytic activity could be preserved at least 14h at 100ºC without any evidence of deactivation. Finally, the material recovered after the catalytic process was characterized by different techniques. X-ray diffraction and Pt L_3-edge XANES spectroscopy show that the crystalline and Pt nature, respectively, were maintained during the catalytic test.

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Direct conversion of Syngas to Olefins over Bifunctional Catalysts: Catalyst design for Increased Olefin Yield and Stability

Glenn Pollefeyt*[1], Vera P. Santos[1], David F. Yancey[2], Davy Nieskens[1], Alexey Kirilin[1], and Andrzej Malek[2]

[1]*Dow Benelux B.V., Herbert H. Dowweg 5, 4542 NM Hoek (The Netherlands)*

[2] *Dow Inc., 1776 Building, Midland MI 48674 (USA)*

[*]*GPollefeyt@dow.com*

Introduction. Over the last years, the development of polyfunctional tandem catalysts, using oxygenates as a chemical intermediate, has gained attention for the direct conversion of syngas to light hydrocarbons.[1, 2] In such a hybrid catalyst, a methanol synthesis component (typically a mixed metal oxide) is coupled with a methanol conversion component (typically a molecular sieve). Recent work showed that for olefin production from syngas, CrZnOx-based bifunctional catalysts are very stable with respect to CO activation, however they suffer from gradual loss in olefin yield because of restructuring of the catalyst [3]. This work studied the technical feasibility of stabilizing the catalyst structure and catalyst performance through the addition of trivalent dopants such as Aluminum, Gallium, Iron and Manganese [4].

Experimental/methodology. Various Fe, Mn, Al and Ga-promoted CrZn-based mixed metal oxides were prepared by co-precipitation. After drying and calcination, the microstructural and physicochemical properties of the catalysts were characterized by XRF, XRD, TPR, XPS, XAS and TEM. The hybrid catalyst was prepared by mixing the desired amounts of mixed metal oxide and SAPO-34 sieve fractions (40-80 mesh). Syngas conversion was performed in stainless steel fixed-bed reactor systems (i.d. 3 - 7.7 mm) at 20 bar and $H_2/CO = 2$, GHSV 1200-3600 h^{-1}. The outlet gas composition was measured using online GC (Maxum).

Results and discussion. The promotion of CrZn methanol synthesis catalysts by the addition of a third element such as aluminum, gallium, iron or manganese can effectively increase the initial C_2-C_3 olefin yield as well as stabilize this high olefin yield over time (Figure 1). Detailed characterization via XAS revealed that incorporating trivalent elements into the spinel phase, stabilizes this structure upon exposure to syngas, leading to higher olefin yield stability. Interestingly, this stabilization effect for iron and mangenese-doped materials is only observed when calcining the materials at low temperature, whereas for aluminum and gallium the stabilization persists up to high calcination temperatures. This work demonstrates the necessity of rational catalyst design, and a perspective will be given on future development options.

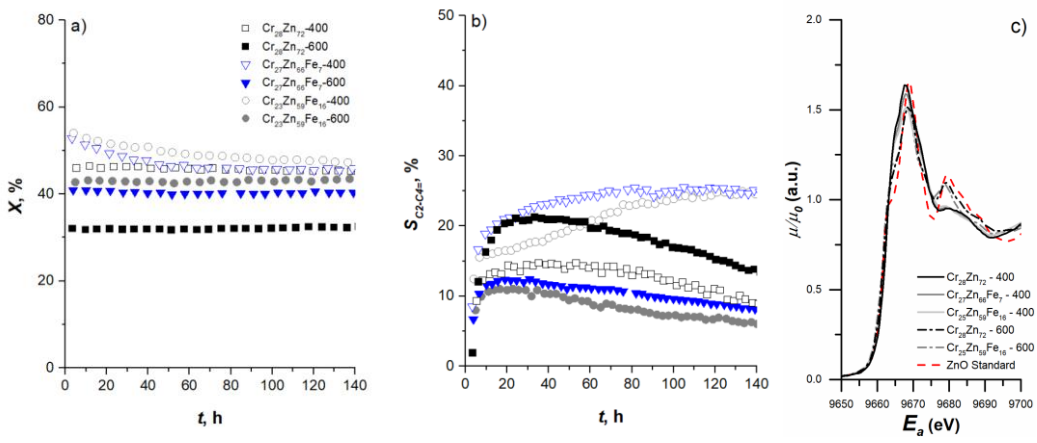

Figure 1: Conversion (a), C_2-C_4 olefin selectivity (b) and XAS spectra (c) for various Fe-doped $CrZnO_x$ oxides.[4]

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Biomass-derived Carbon Supported Cu Electrocatalysts for the CO_2-ElectroReduction

Federica De Luca[1], Tanvir Miah[2], Palmarita Demoro[1], Izuchika Nduka[2], Rosa Arrigo[2], Siglinda Perathoner[1], Gabriele Centi[1], Salvatore Abate[1*]

[1]*ERIC aisbl and CASPE/INSTM, Dpt. ChiBioFarAM University of Messina Viale F. Stagno D'Alcontres 31, Messina, 98166, Italy*

[2]*School of Science, Engineering and Environment University of Salford M5 4WT, Manchester, UK*

[*]*Salvatore Abate, abates@unime.it*

Keywords: Biomass valorization, CO_2 reduction, electrocatalysis, Cu nanoparticles

Introduction. In the context of a circular economy there is the possibility of increasing the economic value of wastes, such as biomass, using them as precursors to carbon supports for electrocatalytic application.
The virtuous recovery of citrus waste forms the basis of the following research studies. It is known that such industrial wastes contain added-value chemical compounds such as phenols , flavoniodes and in particular ascorbic acid, used as a capping agent and reducing agent. This study aims to demonstrate the practicality of directly utilizing citrus waste in a one-pot synthesis of C-supported Cu nanoparticles and their application in CO_2 electroreduction.

Experimental/methodology. Catalysts were prepared by means of microwave-assisted hydro-thermal synthesis; Cu precursor was dissolved in distilled water at 50 °C. Then the peels were finely ground and suspended in the $CuSO_4$ solution and diluted with distilled water afterward thus irradiated with microwaves at 68 °C. The prepared catalysts were thermally annealed in Ar at 500 °C. An ink, was obtained by mixing together catalyst, Nafion, and absolute ethanol by sonication for 2 hours. Then the so prepared ink was deposited on GDL by spray coating. The obtained electrodes, acting as working electrodes, were tested by chronoamperometric detection using a three-electrodes setup cell at two different potential (-1.8, and -2 V vs Ag/AgCl) for 2 hours in a variety of electrolyte (KOH, $KHCO_3$, K_2SO_4) and solution saturated with CO_2.

Results and discussion. The synthesized samples were thermally treated in Ar to enhance the graphitization of the C support, which is required for electrons conduction. The chronoamperometry results show the production of formic acid (FA) and oxalic acid (OA) at both voltages and for both electrocatalysts investigated even if the main product is H_2. The best performances are seen for the Cu-Orange thermally treated electrode with Faradaic efficiency (FE) to FA of about 22% at -2 V vs Ag/ AgCl. The prepared catalyst were characterized by X-ray fluorescence analysis that revealed the presence of : C, N,O,S and Cu. SEM studies highlight a porous support homogeneously decorated with round Cu nanoparticles with an average particle size about 370±60 nm. Finally the XPS analysis of the fresh and thermally treated samples provides more information on the surface chemical composition, consisting mostly of Cu, O, and C. Several differences were found between treated and fresh one samples because the thermal treatment induces marked structural modifications mainly on the C electronic structure. Therefore, it is clear that the use of such waste allows not only their re-use, but shows a double positive effect: I) a support that allows good dispersion of the metal and II) the natural presence of chemical compounds with a reducing function such as ascorbic acid. Concluding, the reported procedure can be applied to the preparation of orange peel derived C-supported metal electrocatalysts for other electrocatalytic reactions of relevance in storage and energy conversion.

Acknowledgments

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Effect of support on methanol selectivity in low-temperature CO_2 hydrogenation to methanol over iridium-based catalysts

Ahmad Alrefaei[1], Atul Bansode[1], Atsushi Urakawa[1*]

[1]Catalysis Engineering, Department of Chemical Engineering, Delft University of Technology, Delft, 2629 HZ, The Netherlands

[*]*A.Urakawa@tudelft.nl*

Introduction: The conversion of CO_2 into a chemical energy carrier, such as methanol (MeOH), is a promising approach to minimize emissions and provide alternative energy sources. The process of converting CO_2 to MeOH is thermodynamically favorable at high pressure and low temperature [1]. However, due to CO_2 stability, a catalytic system is required to activate it at low temperature. Recent research shows that a binuclear iridium (Ir) molecular complex exhibits high activity toward MeOH in low-temperature CO_2 hydrogenation [2]. The high activity is attributed to the Ir species, which forms multiple hydride complexes in the presence of H_2 and are responsible for CO_2 activation via formate formation [2]. In addition, the Ir- based catalysts behavior in terms of the hydrogenation process, interaction with support, activity, and product selectivity can vary depending on the nature of the support [3]. The present work investigates the effect of support in the Ir-based catalytic system in low-temperature CO_2 hydrogenation to MeOH.

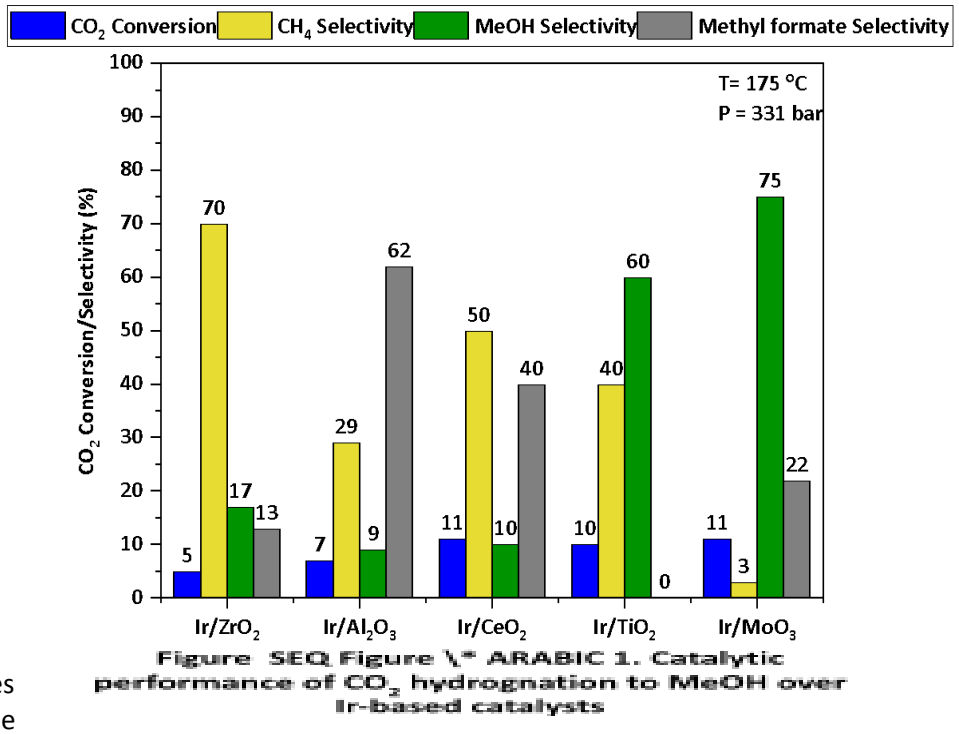

Figure SEQ Figure * ARABIC 1. Catalytic performance of CO_2 hydrogenation to MeOH over Ir-based catalysts

Methodology: 1.5 wt% of iridium metal was impregnated on TiO_2, ZrO_2, MoO_3, Al_2O_3, and CeO_2 to study the catalytic activity and the MeOH selectivity. The activity was examined in a fixed-bed reactor at a temperature of 175 °C, a pressure of 331 bar, and $H_2/CO_2 = 3$.

Results and discussion: The catalytic activity results depicted in Figure 1 demonstrate that the conversion of CO_2 over reducible supports (TiO_2, CeO_2 and MoO_3) is better than non-reducible (ZrO_2 and Al_2O_3), emphasizing the importance of support nature in enhancing CO_2 conversion. However, the support's nature did not have a clear trend on MeOH selectivity as evidenced by the result of both CeO_2 and MoO_3 (reducible supports). Characterization of catalysts by H_2-TPR showed different types of Ir reduction peaks depending on the support used, which highlights the existence of different Ir – support interactions. Furthermore, a noticeable change in product selectivity was observed after several hours, suggesting a possible restructuring of the catalyst. The catalytic performance revealed that Ir/MoO_3 catalyst exhibited remarkable MeOH selectivity at low temperature among others, in comparison with Cu/ZnO/Al_2O_3 (Commercial catalyst), which yielded the same MeOH selectivity at 260 °C and $H_2/CO_2 = 10$ [1].

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Renewable Glycol Production from Glucose Using Novel Ni/WO_x LDH Based Catalysts

Sebastian Kaul[1], Marcus Rose[1*]

[1] *Chemical Technology II, Technical University of Darmstadt, Darmstadt, Germany*
[*] *marcus.rose@tu-darmstadt.de*

Keywords: glucose hydrogenolysis, layered double hydroxides, biomass, hydrogenation

Introduction: In the last decade the use of biomass as a resource for the chemical industry has become of high interest to reduce the dependence of fossil resources and lessen carbon emissions.[1] One important type of biomass is cellulose, which makes up 30-50 % of the biomass.[2] Due to the complex reaction network of the glucose-hydrogenolysis, a catalyst has to be multifunctional to synthesize ethylene glycol (EG) and propylene glycol (PG) effectively. Catalysts have to balance the activity for hydrogenation and retro aldol reaction to produce less hexitols or other side products.[3] Recent developments focused on the use of a hydrogenation metal (e.g. Ni, Ru, Cu, Pd) together with a retro aldol catalyzing metal oxide (e.g. WO_x, La_2O_3).[1,4] In our work, we synthesized a novel, modifiable Ni/WO_x-layered-double-hydroxide (LDH)-based catalyst, which exhibits a high dispersion of active sites. Additionally, different cations could be incorporated into the LDH-Matrix to tailor the activity and selectivity of the final catalyst. Using this catalyst, the kinetics of the reaction network were investigated and structure activity correlations were established.

Experimental/Methodology: The synthesis of the LDH is done using a hydrothermal route with nickel- and aluminium-nitrate. Other cations such as Mg^{2+} or La^{3+} can be incorporated into the LDH-Matrix. Metatungstate is added into the LDH-structure via a pH dependent anionic exchange using diluted HNO_3 as acid. The anion exchanged LDHs are calcined in air, followed by reduction in a hydrogen stream. The catalysts are evaluated in the hydrogenolysis of glucose to EG and PG. The reaction is performed in aqueous solution at 180 °C and 50 bar.

Results and Discussion: The addition of tungstate anions into the LDH-structure was proven by XRD and XRF measurements. Presenting Ni and WO_x contents each with ca. 40 wt%, whereas the WO_x-content was tailored by the choice of pH during the anionic exchange. XRD-measurements of the catalyst showed low intensities, indicating small crystallite sizes. Physisorption experiments revealed an increase of the BET-surface from the LDH (ca. 150 $m^2\ g^{-1}$) to the catalyst (up to 200 $m^2\ g^{-1}$). The high metal loadings together with the high BET-surface areas show the raney-like character of this catalyst system. Ammonia-TPD measurements revealed an increase if the amount and strength of acidic centers, when increasing the WO_x content. TPR-measurements with different WO_x-contents showed a decrease in the reduction temperature with increasing WO_x-content, indicating strong electronic interactions between NiO and WO_x.

In the catalytic experiments, high activities and selectivities towards ethylene glycol were obtained. A study on the WO_x-content showed that an increased WO_x content enhances the glycol yields as well as diminishes hexitol yields. By incorporating Mg into the LDH-structure a decrease in the hydrogenating activity could be achieved, showing/proving the modifiability of this catalyst system. Additionally a thorough kinetic study was performed yielding activation energies as well as information about the reaction system.

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Selective Catalysis using Metal Nanoparticles Confined in Porous Materials

D. Iltsiou[1], M. K. Larsen, J. Mielby[1], S. Kegnæs*[1]

[1]*Department of Chemistry - Technical University of Denmark, Lyngby, Denmark*
**skk@kemi.dtu.dk*

Keywords: catalysis, zeolites, hydrogenation

Introduction.

In spite of the great technological, environmental, and economic interests, general methods for stabilizing metal nanoparticles against sintering are missing. Although for some specific systems, it has been achieved by optimizing the interaction of nanoparticles with a support material or by encapsulation of the metal particles [1-3]. However, these known catalytic systems are, in general, rather expensive and difficult to synthesize, and they cannot be produced on an industrial scale. Therefore, developing novel sintering stable heterogeneous nanoparticle catalysts, which find use in the chemical industry, is very important.

Recently, we have developed several different catalytic systems where metal nanoparticles are confined in different porous materials, including zeolites [3,4,5], porous polymers (POP) [6], and carbon materials [7]. Here, we give an overview of the progress which has been made in the synthesis of metal nanoparticles confined in different porous materials and their application in catalysis. The encapsulation of metal nanoparticles in porous materials often prevents the metal nanoparticle from sintering during a high-temperature catalytic reaction. Furthermore, the porous materials can also contribute actively to the catalytic reaction by improving the catalyst's activity or selectivity, for instance, by controlling the accessible or type of activity sites [3,5]. For instance, we have shown that the metal nanoparticles encapsulated in zeolite materials are only accessible through the pores, which highly favor size-selective reactions [3].

Results and discussion.

We have tested the produced materials as catalysts in different selective oxidation and hydrogenation reactions. For example, nickel-encapsulated nanoparticles in zeolites are highly active in the methanisation of carbon dioxide to methane [5,8]. Furthermore, the location of the metal particles has a great influence on the catalyst activity. Additionally, the encapsulated other metal nanoparticles, like Cu, Ru, Pd, and Pt, were demonstrated to be highly active and selective in various gas-phase reactions, including catalytic oxidation of ethanol to acetaldehyde and hydrogenation of alkenes [9,10]. Furthermore, we have characterized the materials with various techniques, including SEM, in situ TEM, STEM, TEM tomography, XPS, XRF, BET, and XRD, among others.

Acknowledgments

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Superior hydrogenation activity of delafossite-type $CuAlO_2$ catalyst

S. Kikkawa[1*], C. Nagata[1], K. Nitta[2], S. Yamazoe[1,3*]

[1] *Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Tokyo, Japan*

[2] *Japan Synchrotron Radiation Research Institute, SPring-8, Hyogo, Japan*

[3] *Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, Tokyo, Japan*

[*] *kikkawa@tmu.ac.jp*

Keywords: Cu(I)-based catalyst, mixed metal oxide, hydrogenation

Introduction. For most of hydrogenation reactions, the heterogeneous catalysts with expensive noble metals such as Pt, Pd, Rh, and Ru are essential to use. On the viewpoints of elemental strategy, catalysts composed of relatively abundant base metal elements such as Cu and Ni are desirable. Especially, as for the hydrogenation catalyst, H_2 activation at mild condition is requested. For example, Cu/Al_2O_3 catalyst exhibits the activity for hydrogenation of unsaturated hydrocarbons at relatively low temperature and pressures (80°C and 0.4 MPa, respectively)[1)]. The mixed metal oxides containing two-coordinated Cu(I) and secondary metal species (Al, Fe, Nb, Ta, and Ga) are expected to have unique catalytic activity due to their electronic structures and coordination environments. In this study, we synthesized those Cu(I)-based metal oxides by a solid-state reaction (SSR) method and applied them to catalytic hydrogenation of styrene.

Experimental. Mixed metal oxides containing Cu(I), such as $CuAlO_2$, $CuFeO_2$, $CuGaO_2$, $CuNbO_3$, $Cu_5Ta_{11}O_{30}$, and $Cu_{6.78}V_6O_{18.78}$ were synthesized by SSR method according to the literatures[2-4)]. As references, $CuAl_2O_4$ and 0.7wt% Cu-loaded Al_2O_3 were also synthesized by SSR and impregnation method, respectively. The hydrogenation of styrene oxides using various Cu-based mixed metal (catalyst: were carried out in an autoclave toluene 2 30 mg, substrate: 2.7 mmol, solvent: mL, H_2 pressure: 1.0 MPa, reaction temperature: 80°C, reaction time: 18 h).

Fig. 1. Catalytic activities for styrene hydrogenation.

Results and discussion. The XRD patterns showed that the target Cu(I)-based mixed metal oxides containing Cu(I) were synthesized. **Fig. 1** shows the styrene hydrogenation performance of the catalysts at 80°C. Among the Cu(I)-based mixed metal oxides, $CuAlO_2$ exhibited the highest activity, followed by $CuFeO_2$. Two-coordinate Cu(I) oxides, $Cu_5Ta_{11}O_{30}$, $CuGaO_2$, and $CuNbO_3$ showed the activity at 100°C, while $Cu_{6.78}V_6O_{18.78}$ hardly worked for hydrogenation reaction. Cu(II) mixed metal oxide, $CuAl_2O_4$ showed lower activity than $CuAlO_2$. In addition, the low activities were obtained by using γ-Al_2O_3, Cu_2O, CuO, Cu, and Cu/Al_2O_3 as catalysts. XRD patterns suggested that $CuAlO_2$ retained its bulk structure at 80°C. Temperature programmed reduction profile using H_2 suggested that obvious H_2 consumption peaks appeared at higher than 200°C, while there was no reduction peak below 200°C. Cu 2p XPS and Cu L_3-edge XANES spectra of $CuAlO_2$ showed the surface formed Cu(II) species almost disappeared to form Cu(I) species after hydrogenation at 80°C. Thus, we consider that Cu(II) species that partially formed on the surface of $CuAlO_2$ were reduced to active Cu(I) species during the reaction. In conclusion, we found that Cu(I) species on the surface of delafossite $CuAlO_2$ are active species for H_2 activation at low temperature.

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Development of Si-doped Ru/CeLaO$_x$ catalyst for the demonstration of ammonia synthesis

M. Kikugawa[1*], Y. Goto[1], K. Yamazaki[1], Y. Manaka[2], T. Nanba[2], H. Matsumoto[2,3], S. Ookawara[3], A. Sato[4], M. Aoki[1], N. Baba[1]

[1]*Toyota Central R&D Labs., Inc. Nagakute, Aichi, Japan*
[2]*National Institute of Advanced Industrial Science and Technology, Koriyama, Fukushima, Japan*
[3]*Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan*
[4]*Toyota Motor Corporation, Susono, Shizuoka, Japan*
[*]*E-mail: e1542@mosk.tytlabs.co.jp*

Keywords: NH_3 synthesis, Ru catalyst, rare-earth oxide

Introduction

Ammonia (NH_3) is one of the most preferred hydrogen carriers because it can be easily liquefied under mild conditions and its hydrogen density is larger than that of liquid hydrogen [1]. From the viewpoint of using hydrogen derived from renewable energy, the development of an NH_3 synthesis system and catalysts with higher activity than the current Haber–Bosch process under mild conditions is required. Ru/CeLaO$_x$ catalysts exhibit high NH_3 synthesis activity under mild conditions [2]. In our previous study, the substitution of La with Ti in Ru/CeLaO$_x$ catalyst increased the pore volumes, which is the principal factor enhancing catalytic activity [3]. In this study, the effect of Si addition to the Ru/CeLaO$_x$ catalyst to increase the pore volumes and improve the NH_3 synthesis activity was investigated.

Results and discussion

Figure 1 shows the relationship between the rates of NH_3 synthesis and Si addition Y (Y(mol%) = Si/(Ce+La+Si)) to Ru(3wt%)/CeLaO$_x$ catalyst at 350 °C. The rate of NH_3 synthesis exhibited a volcanic-type trend with respect to that of Si addition Y and was the highest at Y = 10. Scannig electrom microscope observations were performed to analyze the morphology of the catalysts (Figure 2). At Y = 10 the catalyst was mesoporous with no observed aggregation of SiO_2 particles. However, at Y = 30, SiO_2 particles were found in the catalyst. The observation suggests that the rate of NH_3 synthesis decreased as the rate of Si addition increased because the Ru on SiO_2 was inactive (Figure 1). The factors for improving the catalytic activity at Y = 10 in terms of the states of Ru and CeLaSiO$_x$ will be discussed.

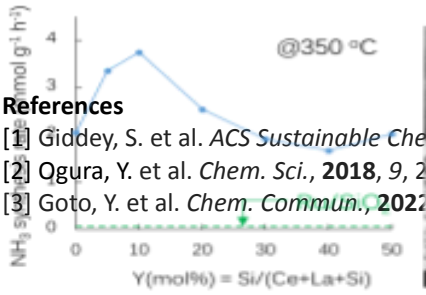

Figure 1. NH_3 synthesis rate of Si-doped Ru(3wt%)/CeLaO$_x$ catalysts at 0.1MPa and 350 °C.

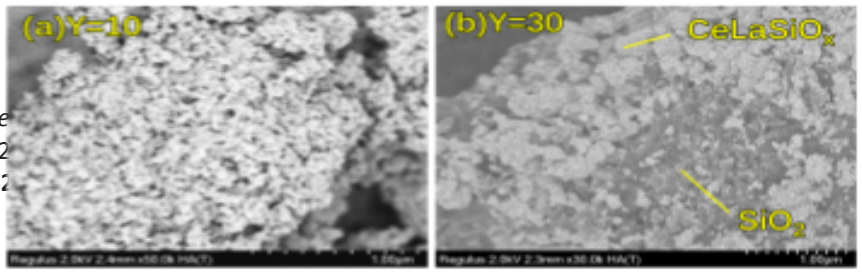

Figure 2. SEM images of Si-doped Ru(3wt%)/CeLaO$_x$ catalysts (a) Y = 10, (b) Y =30.

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Hydrogenation of aromatic LOHC compound over Ru/CeO_2 catalysts with dual functions of heterolytic H_2 adsorption and H_2 spillover

Dongun Kim, Tae Wan Kim, Young-Woong Suh*

Department of Chemical Engineering, Hanyang University, Seoul 04763, Republic of Korea
**Corresponding Author's E-mail address: ywsuh@hanyang.ac.kr*

Keywords: Liquid organic hydrogen carrier, Hydrogenation, Ru–CeO_2 interface, Heterolytic H_2 adsorption, H_2 spillover

Introduction. Liquid organic hydrogen carrier (LOHC) systems, a kind of chemical H_2 storage technology, are based on reversible hydrogenation of H_2-lean molecule and dehydrogenation of H_2-rich one. Benzyltoluene (H_0-BT) is a promising LOHC material with excellent thermophysical properties [1]. Catalytic hydrogenation performance is typically dependent on the ability of H_2 adsorption on the catalyst surface. Heterolytic H_2 adsorption and H_2 spillover can enhance H_2 adsorption capacity [2]. In this respect, CeO_2 containing both basicity and oxygen vacancy is expected to contribute to bringing about both phenomena simultaneously [3,4]. Thus, we herein prepared Ru/CeO_2 catalysts with different basicity and oxygen vacancy, followed by evaluation of their hydrogenation activity and demonstration of both phenomena.

Experimental/methodology. CeO_2 samples were synthesized by precipitation using $Ce(NO_3)_3{\cdot}6H_2O$, followed by aging at 40 to 100 °C, washing, and drying at 105 °C, which are labeled as $CeO_2(x)$, where x indicates the aging temperature. Ru/CeO_2 catalysts were prepared by wet impregnation using $Ru_3(CO)_{12}$ (Ru content: 2 wt%), followed by drying at 105 °C and activation at 500 °C in a H_2 flow, which are denoted as $2Ru/CeO_2(x)$. The hydrogenation activity was measured in a Parr autoclave reactor [5]. Catalytic properties were analyzed by several analysis techniques.

Results and discussion. The first-order rate constants for the conversion of H_0-BT (k_1) and H_6-BT (k_2) of the Ru catalysts in the hydrogenation of H_0-BT became higher with increasing the aging temperature (Figure 1a). Notably, the activity increase was more pronounced between $2Ru/CeO_2(80)$ and $2Ru/CeO_2(100)$ than between $2Ru/CeO_2(40)$ and $2Ru/CeO_2(80)$. In this respect, we selected $2Ru/CeO_2(40, 70, 90, \text{and } 100)$ as representative Ru catalysts for further characterization. The CO_2-TPD profiles showed that the quantity of basic sites as well as the fraction of strong basic sites observed in the range 290 to 298 °C were gradually increased with the aging temperature (Figure 1b). The oxygen storage capacity (OSC), corresponding to oxygen vacancy determined by O_2 chemisorption, was also convergently inclined as the aging temperature increased (Figure 1c). The behaviors of heterolytic H_2 adsorption and H_2 spillover were closely associated with the obtained basicity and oxygen vacancy.

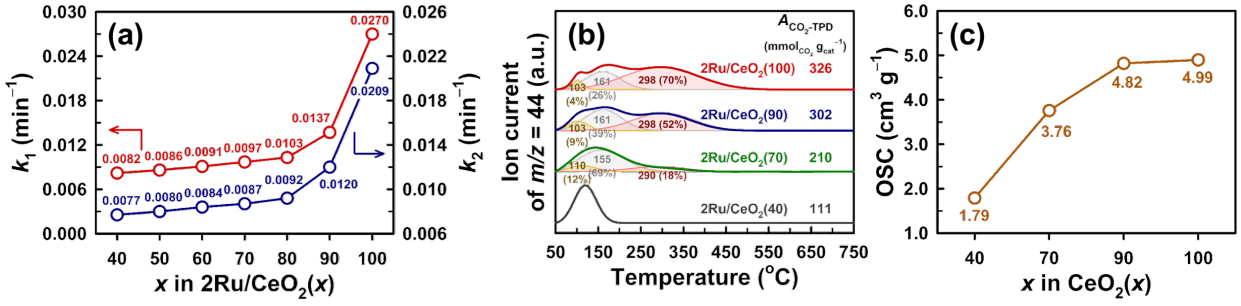

Figure 1. (a) Activites and (b) CO_2-TPD profiles of $2Ru/CeO_2(x)$ catalysts. (c) OSC results of $CeO_2(x)$ samples.

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Biodiesel production using Heteropoly acid and Metal-organic framework Heterogeneous Acid catalyst

Hyungjin Kim[1], Hyeonji Park[1], Joo-Il Park[2*], Won Seok Chi[3*], Yukwon Jeon[1*]

[1] Department of Environmental and Energy Engineering, Yonsei University, 1 Yonseidae-gil, Wonju 26493, Korea
[2]Department of Chemical and Biological Engineering, Hanbat National University, Daejeon 34158, Republic of Korea
[3]Department of Polymer Engineering, Graduate School, Chonnam National University, Gwangju 61186, Korea
[*]jipark94@hanbat.ac.kr(Joo-Il Park) [*]wschi@jnu.ac.kr(Won Seok Ji) [*] ykjeon@yonsei.ac.kr(Yukwon Jeon)

Keywords: Biodiesel, Heteropoly acid, Metal-organic framework, Transestrification, Acid catalyst

Introduction.

Renewable energy sources are now commonly used nowadays. One of them is biodiesel which has advantages like less air pollution by emission gas and non-conversion of conventional diesel engine. Biodiesel is made by plant, animal fat and waste oil. Biodiesel production includes esterification and trans-esterification reaction. Acid catalyst is known for simultainious reaction of esterification and transesterification process with addition of methanol.[1][2] Core-shell acid catalyst of ion-exchanged heteropoly acid(HPA) and metal-organic framework(MOF) is presented. HPA is known for its strong acidity but has high solubility, lack of surface area and low thermal stability. MOF has large surface area and lack of catalytic activity. By combinding two materials we made strong acid catalyst with large surface area and high thermal stability.[3] Catalysts are stabilized by strong chemical bond between HPA and MOF.[4]

Experimental/methodology.

To make core-shell acid catalyst, certain amout of heteropoly acids were used to coat the ZiF-8 particles under stirring condition and dried. The catalysts were used for biodiesel production using reactor. Collected fatty acid methyl ester(FAME) were analyzed using GC.

Results and discussion.

4 catalysts were made by different amount of HPA. To analyze the morphology of core-shell shape, Energy-Filtering Transmission Electron Microscopy (EF-TEM) and TEM Energy Dispersive X-ray Spectrometer (EDS) were used. Example of core-shell shape catalyst is shown in Figure 1. Catalyst of 1:1 weight ratio of HPA and MOF has highest conversion ratio of FAME.

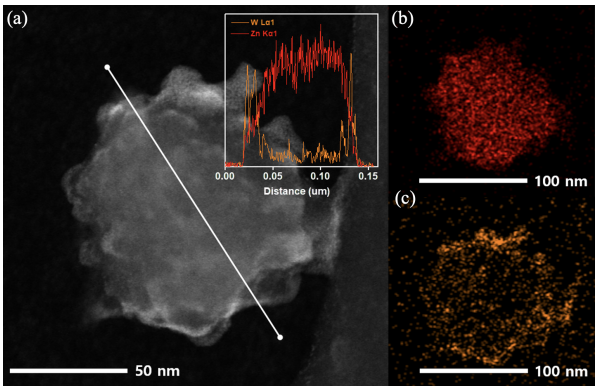

Figure 1. (a) HR-TEM, line EDS of HZS-2, (b) Zn element mapping, (c) W element mapping.

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Biodiesel production using Heteropoly acid and Metal-organic framework Heterogeneous Acid catalyst

Hyungjin Kim[1], Hyeonji Park[1], Joo-Il Park[2*], Won Seok Chi[3*], Yukwon Jeon[1*]

[1] Department of Environmental and Energy Engineering, Yonsei University, 1 Yonseidae-gil, Wonju 26493, Korea
[2]Department of Chemical and Biological Engineering, Hanbat National University, Daejeon 34158, Republic of Korea
[3]Department of Polymer Engineering, Graduate School, Chonnam National University, Gwangju 61186, Korea
[*]jipark94@hanbat.ac.kr(Joo-Il Park) [*]wschi@jnu.ac.kr(Won Seok Ji) [*] ykjeon@yonsei.ac.kr(Yukwon Jeon)

Keywords: Biodiesel, Heteropoly acid, Metal-organic framework, Transestrification, Acid catalyst

Introduction.

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Experimental/methodology.

To make core-shell acid catalyst, certain amout of heteropoly acids were used to coat the ZiF-8 particles under stirring condition and dried. The catalysts were used for biodiesel production using reactor. Collected fatty acid methyl ester(FAME) were analyzed using GC.

Results and discussion.

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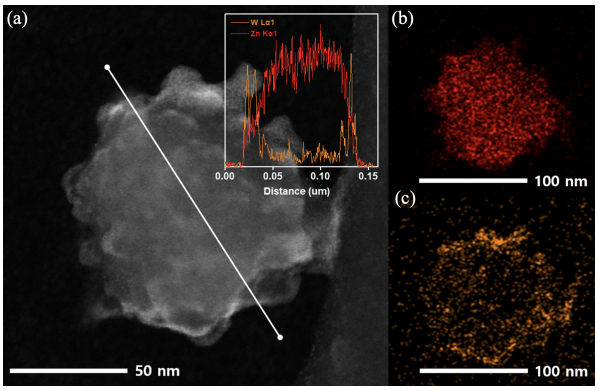

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Highly Selective and Stable Zn promoted precipitated Iron Catalysts for the Production of Linear alpha olefin Via Fischer-Tropsch Synthesis

Kwang Young Kim, Gyoung Woo Lee, Geun Bae Rhim, Min Hye Youn, and Dong Hyun Chun*

Korea Institute of Energy Research, 152 Gajeong-Ro, Yuseong-Gu, Daejeon 34129, Republic of Korea
**cdhsl@kier.re.kr*

Introduction.

Fischer-Tropsch synthesis (FTS: $nCO + \{2n(+1)\}H_2 \rightarrow C_nH_{2n(+2)} + nH_2O$) is an attractive technology for the production of eco-friendly chemicals from waste biomass/plastics or carbon dioxide via syngas ($CO + H_2$) [1]. High temperature-FTS (HT-FTS) is preferred to synthesize olefinic hydrocarbon selectivity with high productivity. However, one of the main drawbacks of HT-FTS is the low stability of catalyst, which requires fused iron-based catalyst with fludized reactor. One feasible approach to overcome this drawback is using precipitated catalysts consisting of Low Temperature-FTS catalysts, such as precipitated iron-based catalysts, with various promoter. In the precipitated catalysts, the activity, selectivity and stability of the desired products is highly dependant on the active phase of iron carbide which mainly controlled by the electronic and structral promoter [2]. Therefore, it is worth drawing a clear correlation between promoter and iron carbide phase for the precision design of HT-FTS catalystsIt is important. One of structural promoter Zn, enhanced catalytic performance by improving dispersion of Fe partcile during the reaction. However, few study has yet reported a clear correlation between iron carbide phase and stability of catalyst, probably due to difficulties in elucidating Fe carbide phase and unexpected interactions between promoter and Fe catalyst. Furthermore, some conclusions are still controversial.

Experimental/methodology.

The Zn promoted catalysts were prepared by precipitation method with different Zn loading (~). We controlled the Zn promotional effect by adding various amount of Zn nitrate precursor. The structural and chemical properties evolution after the reaction of Zn promoted precipitated iron was characterized by Mössbauer and X-ray diffraction analysis. The FTS was performed in a fixed-bed reactor at 305 °C and 1.5 MPa using syngas (H_2/CO = 5.6 NL/$g_{(cat)}$·h) for 114 h after activating the catalysts with syngas (H_2/CO = 1/1, 5.6 NL/$g_{(cat)}$·h) at 280 °C and ambient pressure for 5 h.

Results and discussion.

The addition of Zn promoter improve the catalytic activity and stability of P-Fe (Fig. 1). The stability of Zn promoted catalysts increased as the amount of Zn promoter increased. Especially, when the Zn addition at 9 atomic %, the catalytic LAO in C_6-C_8 weight fraction is maximized (~11%). Further analysis was investigated to confirm the composition of iron carbide phase as the addition amount of Zn. The composition of Fe_7C_3 phase decreased dramatically with increased Zn atomic %. The increase of stability and activity of Zn promoted catalyst highly depend on the composition of iron carbide during the reaction.

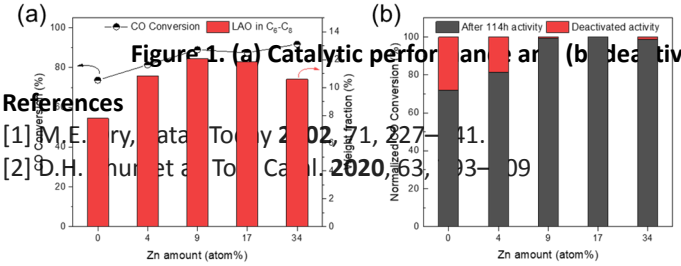

Figure 1. (a) Catalytic perfor an e ar (b dea tivated activity of Zn promoted P-Fe catalysts.

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Doping effect of $Ru/La_2Ce_2O_7$ catalyst in Ammonia Synthesis

Na Young Kim[1], Seok-Ho Lee[1], Seong Ho Lee[1], Kwan-Young Lee[1*]

[1]*Department of Chemical and Biological Engineering, Korea University,*
145, Anam-Ro, Seongbuk-Gu, Seoul, 02841, South Korea
[*]*kylee@korea.ac.kr*

Introduction. Ammonia is increasingly important material as a hydrogen carrier due to its advantages such as ease of transportation, high hydrogen content, and high energy [1]. The currently commercialized ammonia synthesis method is Haber-Bosch method, which synthesizes ammonia under high-temperature and high-pressure reaction conditions to overcome high dissociation energy of N_2 molecules. Since it consumes a lot of energy, catalyst research is needed to synthesize ammonia at mild conditions.
The study was conducted by introducing $La_2Ce_2O_7$, which is known to have high thermal stability and good performance among oxide-based supporters [2-3]. This research aims to enhance the ammonia synthesis activity through oxygen vacancy by doping dissimilar metals to La or Ce ion site of $La_2Ce_2O_7$. Oxygen vacancy is known to be able to accelerate the rate determining step of ammonia synthesis- N_2 dissociation & N-H formation reactions- and has an effect of relieving hydrogen poisoning [4]. In this research, the synthesized catalyst showed good activity in ammonia synthesis reactions, and its structure and characteristics were revealed through various characterization analysis.
Experimental/methodology. $La(NO_3)_3{\cdot}6H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, $X(NO_3)_n{\cdot}mH_2O$, citric acid, $Ru_3(CO)_{12}$, and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Supporter and catalyst were synthesized by impregnation method. For supporter preparation, La, Ce, X precursors and citric acid were stirred in DI water at least 1h, and then solvent was removed by rotary evaporator at 80 °C. After the powder is calcined at 700 °C, 4h (5 °C/min), X-doped $La_2Ce_2O_7$ was synthesized. Then, supporter and Ru metal precursor were stirred in THF at least 1h and solvent was removed by rotary evaporator at 80 °C. After heat treatment at 500 °C to remove CO ligands, X-doped $Ru/La_2Ce_2O_7$ was synthesized.
Reaction tests were performed in fixed bed reactor under 400 °C, 0.1 MPa, H_2/N_2=3, GHSV=72,000 $mL{\cdot}g_{cat}^{-1}h^{-1}$. Generated ammonia was captured in H_2SO_4 trap and its concentration was measured by ammonia detector. Catalyst characterization was done by XRD, CO-chemisorption, TEM, XPS, and etc.
Results and discussion. Catalysts were synthesized differently depending on the amount of X material. No other peaks were observed in XRD data (Fig 1), it can be confirmed that aggregation does not occur and all catalysts were well synthesized.

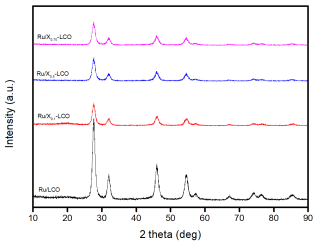

Fig 1. XRD data

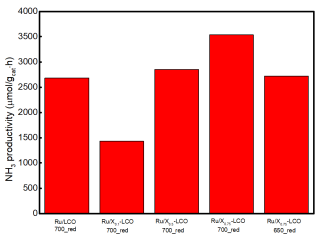

Fig 2. NH_3 synthesis productivity

Before the test, catalysts were reduced under 650 or 700 °C, H_2 60 ml/min. From the result (Fig 2), $Ru/X_{0.75}$-LCO showed the highest catalyst activity in NH_3 synthesis reaction (3,535 $\mu mol{\cdot}g_{cat}^{-1}h^{-1}$). Also, all X-doped Ru catalysts showed more productivity than benchmarking catalyst (Ru/LCO) except $Ru/X_{0.1}$-LCO. According to these results, we can expect that certain amount of X doping enhances catalyst activity in NH_3 synthesis and reduces the reduction temperature of catalyst.

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The catalytic performance of Pd-M/TUD-1 catalysts (where M= Fe, Co, Cu and Ni) in cyclohexene hydrogenation

Manal M. Alshahrani[1*], Mohamed S. Hamdy[1]

[1]*Department of Chemistry, College of Science, King Khalid University, Abha, Saudi Arabia*
[*]*mm.alshahrani@kku.edu.sa*

Keywords: Heterogeneous catalysts; bimetallic catalysts; cyclohexene hydrogenation; Sol-gel method.

Introduction.

Catalytic hydrogenation of cyclohexene has attracted great attention in petrochemical industry to produce cyclohexane which used as starting materials in many processes such as nylon production, pesticides, medicines and fuels [1,2]. The multiple active sites catalysts provide catalytic performance better than single active sites catalysts due to the synergic effect of multiple active sites that provide the following important phenomena's: (i) Increasing species migration on larger surface area to prevent deactivation, (ii) Increasing of the stability of the intermediate on the catalyst surface and then leads to more conversion of these intermediates to products rapidly [3]. Herein, we report a series of supported bimetallic Pd-M/TUD-1 (M = Fe, Ni, Cu, Co) catalysts prepared by sol-gel method for cyclohexene hydrogenation.

Experimental

The sol/gel synthesis technique has been applied to prepare a series of supported bimetallic Pd-M/TUD-1 (M = Fe, Ni, Cu, Co) catalysts. The metal salts (normally nitrate source) have been mixed with the silica source with triethanolamine to prepare homogeneous mixture. This mixture has been treated hydrothermally and calcined to remove all the organic molecules. The prepared catalysts were characterized by several characterization techniques such as FTIR, XRD, SEM, HR-TEM, EDX, UV-Vis, Raman spectroscopy and N_2 physisorption to understand the structure and the properties of the prepared catalysts. The hydrogenation reaction has been carried out in Parr high pressure reactor at 1 bar pressure and 25°C for one hour. Analysis was performed by using GC which equipped with FID detector.

Results and discussion

The characterization results confirmed the formation of mixed nanoparticles of Pd and M (M = Co, Cu, Fe, and Ni) supposed on TUD-1 mesoporous silica. The cyclohexene hydrogenation reaction has been achieved over the bimetallic catalysts Pd-M/TUD-1 as shown in figure 1. Amongst the investigated catalysts the highest conversion of cyclohexane was obtained over Pd-Fe/TUD-1 catalyst in which 13.8% conversion was obtained with 100% selectivity towards cyclohexane. Pd-Ni/TUD-1 exhibited 10.2% conversion, while Pd-Co/TUD-1 catalyzed 6% cyclohexene conversion. The reason for such activity can be related to the higher electronegativity of iron (1.96) compared to Ni (1.88), Cu (1.85) and Co (1.84) while the Pd (1.58) has the lowest electronegativity. The difference between Pd electronegativity and metal promotors enhance the electron getting from Pd species to these metal promotors (Fe, Ni, Cu and Co) in different degrees. The increasing in electron-deficiency Pd^{δ} $^{\delta+}$ sites lead to strong interaction with electron-rich π π electrons of double bond in cyclohexene and the metal promotors increase the adsorption of cyclohexene on the catalyst surface and a high hydrogenation rate has been achieved. The detailed characterization results as well as the optimization of the catalysts will be discussed during the presentation.

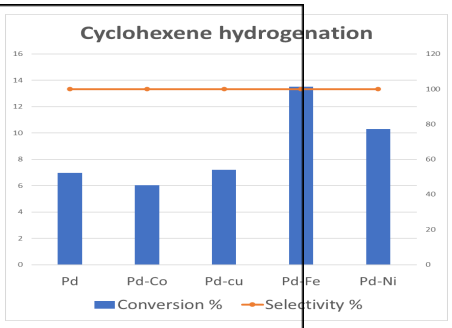

Figure 1. Cyclohexene hydrogenation over Pd-M/TUD-1 catalysts

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Effect of Alkyl Chain Length on the Structures of Dendritic Silica Supported Palladium Catalysts for Hydrogenation of Furfural

Ye Eun Kim[1,2], Panseong Kim[1], Gangmin Kim[1], Man Sig Lee[1*]

[1]*Korea Institute of Industrial Technology, Ulsan, Republic of Korea*
[2]*Korea University, Seoul, Republic of Korea*
[*]*lms5440@kitech.re.kr*

Keywords: Dendritic silica, Alkyl chain, Furfural hydrogenation, Pd/SiO_2

Introduction. In general, it is widely accepted that the catalytic activity can be significantly affected by the support properties, such as pore size, porous structures, and acid-base properties [1-3]. Dendritic silica with three-dimentional porous structures can lead to higher mass transfer and catalytic activity compared to traditional mesoporous silicas (MCM-41, SBA-15, KIT-16). Herein, we prepared the dendritic silicas with different structures and investigated the effect of supports on the catalytic activity.

Experimental/methodology. The dendritic silicas were hydrothermally treated at 120 ℃ for 6 h with varying the different kinds of alcohols as co-solvents. The synthesized powder was filtered, washed with acetone and distilled water, and dried overnight. The dried samples were calcined at 550 ℃ for 6 h to remove the surfactants. The dendritic silica supported Pd catalysts were prepared by chemical reduction method and the catalytic activity was conducted via furfural hydrogenation.

Results and discussion. Dendritic silicas with different dendritic structures could be successfully prepared by using various alkyl chain-containing alcohols as co-solvents. The dendritic silicas exhibited distinct morphologies, revealing a correlation between catalyst surface area and activity. When the longer alkyl chain-containing alcohols were used, the larger wall distance was observed, leading to the increase in the specific surface area and Pd dispersion. This result exhibited that the wall distance was affected by the hydrophobicity of oils and the affinity of cationic surfactant and cyclohexane. The longer alkyl chain alcohol has a tendency with hydrophobicity which interacts with cyclohexane (a hydrophobic solvent). Various dendritic silicas were used as catalyst supports, and the effect of supports on the furfural hydrogenation was observed. The larger specific surface area and wall distance showed the increase in the initial reaction rate in 1 h as well as an improvement in selectivity toward tetrahydrofurfuryl alcohol. The larger specific surface area and wall distance resulted in an increase in the initial reaction rate within 1 hour, as well as an improvement in selectivity. This improvement was attributed to the enhanced specific surface area, providing a uniform Pd dispersion area for better interaction with reactants. In conclusion, the dendritic silica-based catalyst with a larger wall distance improved catalytic activity due to its larger specific surface area and higher mass transfer efficiency.

Acknowledgments
This research was supported by Korea Institute of Industrial Technology (EH-23-0002 and JA-23-0015).

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Ba-Si Oxynitride-Hydride as a Transition Metal-Free Catalyst for Ammonia Synthesis

M. Kitano*, Z. Zhang, M. Miyazaki, H. Hosono

[1] *MDX Research Center for Element Strategy, International Research Frontiers Initiative, Tokyo Institute of Technology, Yokohama, Japan*
**kitano.m.aa@m.titech.ac.jp*

Keywords: Oxynitride-hydride, ammonia synthesis, anion vacancy

Introduction. Catalytic ammonia synthesis is vital for production of fertilizer, which is needed to produce food for the world's expanding population. Dissociation of N_2 and H_2 to form ammonia generally occurs on the surface of supported transition metal (TM) particles such as Fe and Ru. The ammonia formation reaction can be promoted by electron donating support. Recently, combination of TM and hydride materials has been demonstrated to function as efficient catalysts for ammonia synthesis under mild reaction conditions.[1,2] TMs, however, are still irreplaceable as active centers for N_2 dissociation in most cases. In the present study, we fabricate a novel Ba-Si oxynitride-hydride with high concentration of H^- and N^{3-} ions via low-temperature solid-state reaction, and demonstrate its excellent ability for TM-free N_2 activation to produce NH_3 continuously under mild conditions.

Experimental/methodology. $Ba_3SiO_{5-x}H_yN_z$ powder was prepared by a solid-state reaction of SiO_2 with $Ba(NH_2)_2$ at 400-700°C for 12 h under NH_3 atmosphere. XRD, FT-IR, HAADF-STEM, XPS, XAFS, FT-IR, TPD, N_2 adsorption-desorption were used to characterize the catalysts. Ammonia synthesis reactions were conducted in a fixed bed flow system and the produced ammonia was trapped in 5 mM sulfuric acid solution and the amount of NH_4^+ generated in the solution was determined using ion chromatography.

Results and discussion. $Ba_3SiO_{5-x}N_yH_z$ without any TM site shows continuous ammonia production at ca. 0.37 mmol g_{cat}^{-1} h^{-1} without degradation in activity during the 150 h test at 400°C and 0.9 MPa. The total amount of ammonia was estimated to be ca. 5.25 mmol (per 0.1 g of catalyst), which is much higher than that of the amount of N^{3-} (0.16 mmol) and H^- (0.37 mmol) in the lattice, and indicates the ammonia produced originates from the activation of molecular N_2 and H_2 but not from the decomposition of $Ba_3SiO_{5-x}N_yH_z$. Neither Ba_3SiO_5, $Ba(NH_2)_2$ nor SiO_2 powder exhibits activity for ammonia synthesis, even at temperatures up to 540°C, while the $Ba_3SiO_{5-x}N_yH_z$ powder can effectively activate N_2 to produce ammonia at temperatures down to 300°C (0.04 mmol g^{-1} h^{-1}, Fig. 1). The lattice heteroanions of H^- and N^{3-} are easily desorbed to form a high concentration of V_a sites with confined electrons, where N_2 can be captured and directly activated to ammonia in the absence of any TM site. FTIR experiment revealed that $Ba_3SiO_{5-x}N_yH_z$ exhibits an N_2 adsorption peak centered at around 2016 cm^{-1}, which is much lower than that of conventional Ru catalysts and the reported electride-based catalyst (Ru/C12A7:e^-, 2176 cm^{-1}). This result indicates that electrons trapped at the surface anion vacancy sites directly interact with N_2 and facilitate π-back donation into the antibonding orbital of the N_2 molecule, which leads to a shift of the N_2 adsorption band.

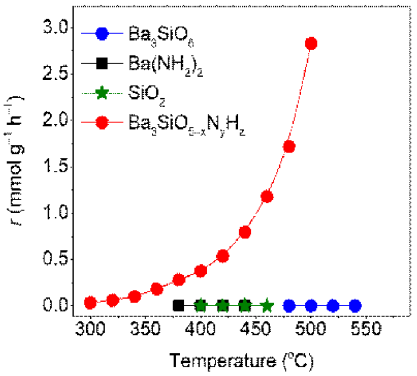

Fig. 1 Temperature dependence of the ammonia synthesis rate over various materials without TMs.

Acknowledgments

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Plasma-Supported Catalytic Synthesis of Light Hydrocarbons

J. Titus[1,2] , T. Lorenz[2], M. Drößiger[2], O. Kuschel[1], C. Koch[2*]

[1]*Institute of Chemical Technology, Universität Leipzig, Leipzig, Germany*
[2]*enaDyne GmbH, Turmhofstraße 1, 09599 Freiberg*
[*]*CK@enadyne.de*

Keywords: plasma catalysis, light hydrocarbons, CO_2 conversion

Introduction. Methane and carbon dioxide count as two main contributors to the greenhouse effect. Hence, their emission needs to be reduced. While CO_2 as thermodynamically highly stable molecule is widely inactive, recent research focuses on its hydrogenation. A promising, but thermodynamically challenging route is the dry reforming of methane in which CO_2 and CH_4 are converted at elevated temperatures to form synthesis gas. An alternative pathway to thermal catalysis is the excitation of the reactants in a plasma [1]. Here, we report the catalytic synthesis of light hydrocarbons and oxygenates from CO_2 and CH_4 in a dielectric barrier-discharge (DBD) reactor. Besides a variation of the catalyst, the effect on plasma parameters and product gas composition is investigated.

Experimental/methodology. An equimolar stream of CO_2 and CH_4 is lead through a self-build V-DBD reactor in which plasma is generated at temperatures up to 573 K. The plasma is ignited using a novel electrode material. The reaction products are studied via GC. To enhance the selectivity toward defined reaction products, the catalyst powder is introduced within the plasma according to in-plasma catalysis. Since the reaction is conducted within the plasma, its effect on catalysts is studied by investigating varying active metal loaded alumina-supports. These were prepared eighter by sol-gel method [2] or via incipient wetness-impregnation, to distinguish additionally the effect of preparation method and catalyst characteristics on the resulting plasma.

Results and discussion. The novel electrode material allows the generation of a plasma, which is indicated to be a highly diffusive plasma-mode (Fig. 1). Further, the determination of energy input needed to ignite the plasma, even in presence of CH_4 and CO_2 suggest, that the excitation of reactants follows the so called ladder climbing pathway. Hence, the dissociative pathway is expected to be suppressed. Besides the reduction of energy input into the plasma, the reaction product distribution is limited favoring, e.g. C-C coupling.

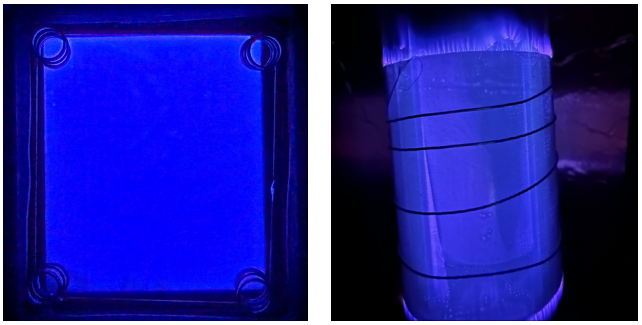

Figure 1: Image of the plasma generated using the novel electrodes in presence of a catalyst, or planar (left) and tubular (right) catalyst studies.

By exciting CO_2 and CH_4 within the plasma, resulting reaction products were found to be short chained ($\leq C_4$) hydrocarbons. Hence the formed, excited species follow a C-C coupling mechanism. The presence of alcohols leads to the conclusion, that not only CH_4 participates in the reaction, but also the CO_2 is inserted within the reaction products.

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Metal Organic Frameworks Derived Tunable Supported Nickel Catalysts for Methane Dry Reforming

Eswaravara Prasadarao Komarala[1], Aasif Asharafbhai Dabbawala[1,2], Messaoud Harfouche[3], Nikolaos Charisiou[4], Dalaver H. Anjum[2,5], Mark A. Baker[6], Maria Goula[4] and Kyriaki Polychronopoulou[1,2]*

[1,2,5]*Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates;* [3]*Synchrotron-light for Experimental Science and Applications in the Middle East (SESAME), Allan, Jordan;* [4]*University of Western Macedonia, Koila, Greece;* [6]*University of Surrey, Surrey, United Kingdom;*
**Corresponding Author's E-mail address: kyriaki.polychrono@ku.ac.ae*

Keywords: metal organic frameworks, supported catalysts, dry reforming of methane, strong metal-support interactions.

Introduction. Dry reforming of methane (DRM) using carbon dioxide (CO_2) is an inimitable approach for eliminating both greenhouse gases, methane and CO_2, emissions while producing synthesis gas which further can be converted to useful fuels.[1] However, the industrialization of DRM has been limited due to sintering and carbon accumulation (coking) issues related to the catalysts under the harsh reaction conditions.[2] Here, we developed a new methodology for producing supported nickel-based catalysts with tunable metal-support interface for DRM using metal organic frameworks (MOFs) as precursors of the catalyst components (both metal and support).

Experimental/methodology. The MOFs derived catalysts were obtained by calcining coalesced (through sonication) Ni-BDC and La-BDC MOFs at different temperatures. The obtained catalysts were characterized using XRD, SEM, TEM, temperature programmed physisorption and chemisorption. Finally, the catalytc activity was tested towards DRM at extreme environments of 800 °C and high gas hourly space velocities.

Results and discussion. In this work, we produced tunable supported Ni-based catalysts consists of strong metal-support interactions (SMSIs) for dry reforming of methane using MOFs as precursors for synthesizing Ni/NiO nanoparticles supported on different lanthanum phases (La_2O_3, $La_2O_2CO_3$, and $La(OH)_3$).

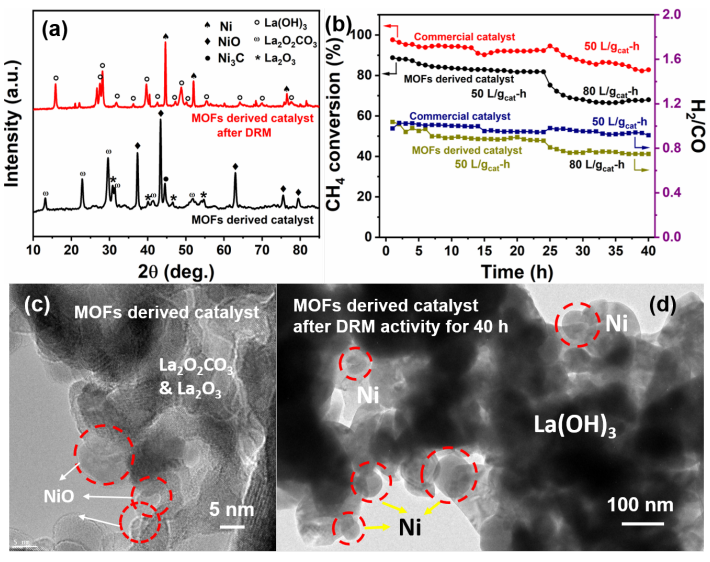

Figure 1: (a) XRD patterns of as synthesized and spent MOFs derived catalyst, **(b)** comparison of DRM activity of MOFs derived catalyst with commercial catalyst; TEM images of **(c)** as-synthesized and **(d)** after DRM activity of MOFs derived catalyst, respectively.

Figure 1a shows the phases formed before and after DRM activity of the MOFs derived catalyst. The DRM activity in **Figure 1b** demonstrate that the MOFs derived catalyst exhibited stable and high CH_4 conversion rates even at high gas hourly space velocities. Although the commercial catlayst has shown high CH_4 conversion rate at initial hours, a continuous decrease in conversion rate was observed at lower GHSV, which lacks the stable catalytic activity. The TEM images shown in **Figure 1c** and **1d** reveals that the MOFs derived catalyst exhibit SMSIs with no coking and minimal sintering (bottleneck of industrializing the DRM reaction). Since the supported catalysts with these qualities are highly desirable for the industries, the present synthesis can open up avenues to produce supported catalysts for the energy production sector.

Acknowledgments. *The authors acknowledge Khalifa University through the CIRA 2020-077. The authors also thank Ms. Swati Singh and Prof. Michael Gozin for their help in synthesis and measurements.*

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Metal nanoparticles on 3D graphene-like nitrogen-doped zeolite-templated carbon for hydrogenation reactions

Nikola Kostkova[1,2], Jaroslava Moravkova[1], Radim Pilar[1], Galina Sadovska[1,2], Alena Vondrova[1], Ivan Jirka[1], Petr Sazama[1*]

[1]*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic*
[2]*University of Pardubice, Studentska 95, 532 10 Pardubice, Czech Republic*
[*]*Petr Sazama (petr.sazama@jh-inst.cas.cz)*

Keywords: nitrogen-doped carbon, zeolite-templated carbon, metal clusters, catalyst support, hydrogenation reactions

The electronic properties of metal catalysts are modulated by the interaction of the metal clusters with a catalyst support. Due to the chemical intertness of the carbon surface basal plane, the electronic interaction between carbon supports and the noble metal is weak. To provide stronger interaction, this study exploited functionalization of 3D graphene-like zeolite-templated carbon materials with nitrogen heteroatoms to create nitrogen-containing surface functional groups and defective centers. Catalytic activity, selectivity and stability can be adjusted by modulation of the metal–metal coordination in 3D graphene-like zeolite-templated carbon materials.

3D graphene-like microporous carbons (β-(N)carbon and Y-(N)carbon) were prepared using the beta (*BEA) and faujasite (FAU) zeolites in the H^+ form of the molecular Si/Al ratios 4 – 12 as hard templates. Chemical vapour deposition was performed to execute the carbonization process with the appropriate carbon and nitrogen precursors. Pyrrole as a nitrogen precursor was used for incorporation of the pyridinic and pyrrolic groups. The use of acetonitrile as a carbon and nitrogen precursor led to the formation of graphitic nitrogen. Typical procedure for carbonization consists of a carbon deposition with diluted stream of the carbon and nitrogen precursor at 700 - 850 °C and sample heat treatment in a stream of nitrogen at 900 °C. The zeolite/carbon composite was leached in aqueous solutions of hydrofluoric and hydrochloric acids to remove zeolite template. The impregnation with organic solutions of corresponding element salt in hexane or acetylacetone as solvents allowed the introduction of metal clusters (Pt and Pd) into carbon materials.

Hydrogenation of 1,3-butadiene, 1-hexyne and benzene (as model compounds) allowed the evaluation of the effects of increased interaction with the support and reduced metal–metal coordination on activity, selectivity and stability. The conventional metal supported catalysts were used to compare activity and stability. The method enabled an adaption of the electronic properties and the dispersity of active metal clusters on the (N)carbon catalysts to increase the reaction rates and to tailor the activity, selectivity and stability of the catalyst.

Acknowledgments
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Engineering Exsolved Catalysts for CO_2 Utilization

S. A. Ali[1], M. Safi[1], L.-P. Merkouri[1], S. Soodi[1], A. Iakovidis[2], M. S. Duyar[1], D. Neagu[3], T. Ramirez Reina[4], K. Kousi[1*]

[1]*School of Chemistry and Chemical Engineering, University of Surrey, Guildford, UK*
[2]*School of Mechanical Engineering Sciences, University of Surrey, Guildford, UK*
[3]*Department of Chemical and Process Engineering, University of Strathclyde, Glasgow, UK*
[4]*Department of Material Sciences Institute of Seville, University of Seville-CSIC, Seville, Spain*

[*]*k.kousi@surrey.ac.uk*

Keywords: carbon dioxide utilisation, exsolution, dry reforming, greenhouse gases, efficient catalysts

Introduction. Innovating technologies to efficiently reduce carbon dioxide (CO_2) emissions or covert it into useful products has never been more crucial in light of the urgent need to transition to a net-zero economy by 2050. The design of efficient catalysts that can make the above a viable solution is of essence. Many noble metal catalysts already display high activity, but are usually expensive. Thus alternative methods for their production are necessary to ensure more efficient use of noble metals. Exsolution has been shown to be an approach to produce strained nanoparticles, stable against agglomeration while displaying enhanced activity[1]. Here we explore the effect of a low level of substitution of Ni into a Rh based A-site deficient titanate aiming to investigate the formation of efficient, low loading noble metal catalysts. We show that this design principle not only fulfils a major research need in the conversion of CO_2 but also provides a step-change advancement in the design of tandem catalysts.

Experimental/methodology. The perovskite oxide powders were synthesized by a modified solid-state synthesis. In order to exsolve particles, the samples were reduced at temperature in a controlled atmosphere furnace, under continuous flow of H_2 with heating/cooling rates of 5 °C/min. To measure the effect of reduction temperature on the exsolution of Rh particles, 800 °C and 1000 °C with a dwell of 10 h were used. The crystalline phase components of all freshly prepared and reduced samples were investigated using X-ray diffraction, scanning and transmission electron microscopy were used to study the nano and microstructure of the materials and an Image processing program (ImageJ) was used to carry out the particle morphological analysis. Thermogravimetric analysis and temperature programmed oxidation were carried out to measure extent of reduction and carbon deposition. Catalytic testing was done under a reactant gas mixture of (12.5% CH_4: 12.5% CO_2: 75% N_2) from 600 to 800 °C.

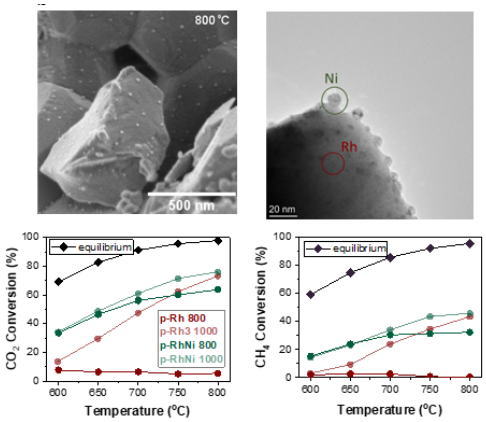

Figure 1: a. SEM and TEM images of the exsolved samples b. Catalytic testing

Results and discussion. The results here (fig1) demonstrate that doping of Ni could indeed enhance its exsolution capabilities driving more Rh particles towards the surface of the perovskite, also demonstrating significantly improved catalytic activity in DRM reaction compared with its undoped counterparts reduced

at the same temperature. However, temperature still seems to be a greater driving force for exsolution of cations from a perovskite lattice. Nevertheless, we demonstrate that there might be a way to produce catalysts with distinct active sites that could be employed for what we normally call tandem catalysis. These materials are produced in a single step and could avoid any deactivation mechanisms usually caused by the degradation of two or more catalysts put together in an assembly method.

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Pt-, Ru- modified H-Beta, H-Y zeolites and H-MCM-41 mesoporous material extrudate catalysts for synthesis of menthol from citronellal: Influence of structures, acid sites Pt- and Ru- metal nanoparticles size distributions

[1]N. Kumar, [1]Z. Vajglova, [1]P. Mäki-Arvela, [1]K. Eränen, [2]M. Peurla, [1]D. Yu. Murzin, [1]Åbo Akademi University, Laboratory of Industrial Chemistry and Reaction Engineering, Faculty of Science and Engineering, Henriksgatan 2, FI-20500 Turku/Åbo, Finland, [2]Turku University, Institution of Biomedicin, FI-20140, Turku, Finland

Increased demand of menthol for applications in the pharmaceutical, medicinal, food and fragrance industry requires enhancing the current synthetic route of production. Utilization of different catalytic formulations and optimization of reaction conditions are important for enhancing the production of synthetic menthol. In the present research the main aims were synthesis and physico-chemical characterizations of Pt-, Ru- modified H-Beta, H-Y zeolites and H-MCM-41 mesoporous material extrudate catalysts. Further aim was application of these acidic, Pt- and Ru- modified extrudates for the production of menthol from citronellal. Pristine H-Beta, H-Y extrudates were synthesized using bentonite binder with varying compositions. H-MCM-41 mesoporous material extrudate was synthesized using colloidal silica bindzil binder. Pt-, Ru- modifications were carried out using *in-situ* and post synthesis modifications. Physico-chemical characterization of pristine H-Beta, H-Y, Pt-H-Y, Pt-H-Beta (Fig 1), Ru-H-Beta, Ru-H-Y (Fig 2) and Ru-MCM-41 revealed that method of introduction of Pt-, Ru- in the extrudates influenced metal nanoparticle size distribution, location and dispersion. The physico-chemical characterizations were carried out using several instruments such as XRD for phase purity and N_2-physisorptions for textural properties, surface area, pore volume and pore size distributions. Pt-, Ru- metal nanoparticles size distributions were measured using TEM and SEM was utilized for determination of morphological features of the extrudates. Evaluations of the catalytic properties of the Pt-, Ru- modified extrudates in the transformation of citronellal to menthol were carried out in trickle bed reactor at pressure 10 bar, temperature 70 ^{o}C. The catalysts were pretreated in flow of hydrogen at 350 ^{0}C prior to catalyst evaluations. The zeolite structure, amounts of Brønsted and Lewis acid sites of pristine H-Beta, H-Y, Pt and Ru modified H-Y, H-Beta extrudates were observed to influence the conversion of citronellal and selectivity to menthol. Furthermore, Pt- and Ru- metal nanoparticle size distributions, locations and dispersion were also observed to influence the conversion of citronellal and selectivity to menthol.

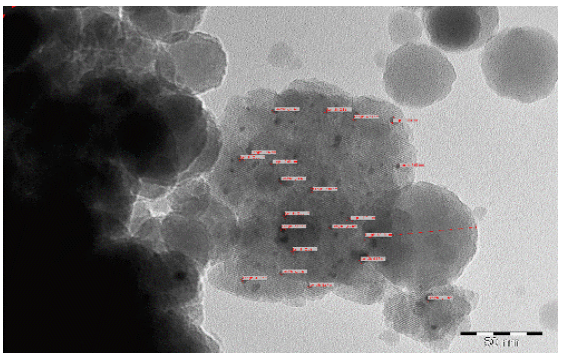

Fig1.

Fig. 1. TEM Pt-H-Beta extrudate

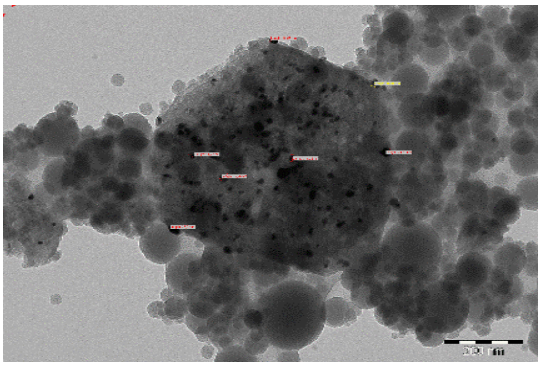

Fig 2.

Fig.2. TEM Ru-H-Y extrudate

CuFe@zeolite catalysts selectively hydrogenate C≡C triple to C=C double bond

A. Kurbanova*, J. Přech, S. Kurucová, M. Mazur, D. Zákutná

Dept. of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Albertov 6, Prague 2, Czech Republic
**Corresponding author: anastasia.kurbanova@natur.cuni.cz*

Keywords: Reductive demetallation, zeolite, hydrogenation, hydrogenolysis, triple bond, ester

Introduction.

Selective reduction of C≡C triple to C=C double bond, avoiding full saturation of the hydrocarbon, is an important reaction in many petrochemical as well as fine chemistry processes. Typical catalysts for this reaction are based on palladium, sometimes partially poisoned with lead (Lindlar catalyst). Nevertheless, application of noble metals as well as heavy metals raises environmental and cost issues since the production of noble metals is costly and energy-intensive while, e.g., lead compounds are poisonous. Thus, replacing these metals with other inexpensive transition metals such as Fe, Cu, and Zn without sacrificing the selectivity, would necessarily reduce their production costs as well as the ecological footprint. Encapsulating the metallic particles in a zeolite carrier could then provide and stabilize fine dispersion of the metallic particles.

In this contribution, we present preparation and catalytic performance of CuFe and CuZn bimetallic nanoparticles encapsulated into zeolite channels in the partial hydrogenation of C≡C bond. We also demonstrate potential of these catalysts in ester hydrogenolysis.

Experimental/methodology.

The CuFe@zeolite and CuZn@zeolite composite catalysts are produced by reductive demetallation of Fe-MFI or Zn-VET zeolites followed by ion-exchange into Cu^{2+} forms. Reductive demetallation means a transformation of framework Fe^{3+} and Zn^{2+} metal ions into metallic nanoparticles, where the metal has oxidation state 0, under H_2 atmosphere at high temperatures [1,2]. The reductive demetallation is accompanied by the formation of defects in the zeolite structure nevertheless, the zeolite structure does not collapse. Catalytic hydrogenation of ethynyl anisol to vinylanisol was carried out in heptane at 5 bar H_2 pressure and 50°C. Hydrogenolysis of methyl laurate was performed at 100 bar H_2 at 250°C.

Results and discussion.

The CuFe@MFI (3% wt. Cu, 2% wt. Fe) and CuZn@VET (3% wt. Cu, 7% wt. Zn) gave 21% and 16% conversion after 3 h, respectively, in 3-ethynylanisole hydrogenation. The Lindlar catalyst (5% et. Pd, poisoned with Pd) gave 100% and a 2% $Pd/SiO_2.Al_2O_3$ reference provided 85% conversion. Nevertheless, at 20% conversion, CuZn@VET provided 84% selectivity towards 3-vinylanisole and CuFe@MFI 80% selectivity. These selectivity values are comparable with the selectivity of the Lidlar catalyst (94 % at 22% conversion) under the same conditions while $Pd/SiO_2.Al_2O_3$ exhibited 85% selectivity. Taking into account the above cost and environmental issues, the CuFe and CuZn composite catalysts represent a promissing alternative to the state-of-the-art Pd based catalysts.

CuZn mixed oxides are also established catalysts of ester hydrogenolysis. Similarly, the CuFe@MFI catalyze methyl laurate hydrogenolysis to lauryl alcohol and methanol. In contrast to the CuZn mixed oxides, it also exhibits significant transesterification activity (yielding lauryl laurate with 60% selectivity at 50% conversion) whose origin is likely from remaining share of acid sites in the catalyst. Thus, tuning the demetallation conditions should control the transesterification activity.

Acknowledgments

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Catalytic combustion of volatile organic compounds over transition metal oxides deposited on zeolite-decorated ceramic monoliths

Anna Rokicińska[1], Marek Drozdek[1], Magdalena Żurowska[1], Elżbieta Bogdan[2], Adam Węgrzynowicz[2], Piotr Michorczyk[2], Piotr Kuśtrowski[1*]

[1]*Faculty of Chemistry, Jagiellonian University, Krakow, Poland*
[2]*Institute of Organic Chemistry and Technology, Cracow University of Technology, Krakow, Poland*
[*]*piotr.kustrowski@uj.edu.pl*

Keywords: catalytic combustion of volatile organic compounds, transition metal oxide catalysts, ceramic monoliths, 3D printing, MFI zeolite washcoat

Introduction. The emission of volatile organic compounds (VOCs) into the atmosphere remains a serious problem that poses both an environmental threat and a negative impact on human health [1]. Extensive scientific research has led to the development of several effective methods for the VOCs elimination. Among them, the catalytic combustion has appeared to have the greatest potential for the removal of organic pollutants from a very dilute air stream. However, passing the polluted air through a catalytic converter at a high volumetric flow rate may result in an observed pressure drop in the bed constructed of powder catalyst. This disadvantage disappears when monolithic reactors are used. In the presented work, the application of technique of manufacturing ceramic monoliths supported by 3D printing was proposed. As the active phase, transition metal oxides were used, which are less expensive and more resistant to the presence of heteroatoms than noble catalysts.

Experimental. The ceramic monoliths were obtained by the templating technique using 3D printed resin-based matrices. The prepared resin templates were modified using a paste consisting of α-Al_2O_3 powder dispersed in a sodium silicate solution and calcined at 850 °C [2,3]. Afterward, the surface of the monolith was coated with a MFI zeolite layer to increase porosity and thus develop the specific surface of support. Finally, different amounts of precursors of the active phase (i.e. single Co, Cu, and Mn oxides, as well as their mixtures) were introduced by the wet impregnation and coprecipitation methods. The calcined materials were characterized in terms of morphology (SEM), chemical composition (XRF), structure (XRD), texture parameters (N_2 adsorption), surface composition (XPS), reducibility (H_2-TPR), as well as were tested as catalysts in the total oxidation of toluene under various conditions.

Results and discussion. Preliminary catalytic tests revealed that a major difficulty in maintaining stable operation of the catalytic system working in the total oxidation of toluene is a large amount of heat released during the exothermic reaction. To avoid this negative effect, we proposed the use of a catalytic bed consisting of a cascade of variously modified short monoliths instead of one long monolith. In the developed system, the heat released in the first part of the catalytic bed (active at lower temperature) is used to heat the reacting mixture to the temperature required for activity in the next part of the same bed (active at higher temperature). Various arrangements of short monoliths, differing in composition, were tested. The best catalytic results were achieved over properply arranged the monolith systems consisting of individual CuO or Co_3O_4 oxides, as well as mixed Cu-Mn-O. Furthermore, it was proven that the catalytic activity in the studied catalytic system is correlated with the mobility of lattice oxygen involved in the oxidation process according to the Mars–van Krevelen mechanism.

Acknowledgments
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Fe-modified $SrTiO_3$ and Mn-modified $SrTiO_3$ as materials for environmental catalysis

A. Łącz*, P. Gwóźdź, N. Moskała, S. Komarek, E. Drożdż

AGH University of Science and Technology in Krakow, Faculty of Materials Science and Ceramics, Poland
**alacz@agh.edu.pl*

Keywords: Mn-doped $SrTiO_3$, Fe-doped $SrTiO_3$, catalyst, NOx reduction

Introduction. There has been a growing interest in the use of perovskite-based materials in environmental catalysis in recent years. One of the concepts is the application of strontium titanate ($SrTiO_3$) doped with *d*-metals for NOx reduction by ammonia (NH_3-SCR). The possibility of incorporation of manganese or iron into the Ti-sublattices in the $SrTiO_3$ perovskite structure can be controlled by introducing non-stoichiometry into Sr-sublattice. Thus, the materials with various levels of non-stoichiometry and various Fe/Mn content were obtained and studied to evaluate the impact of strontium deficiency on the structure and catalytic properties of Mn-doped $SrTiO_3$ and Fe-doped $SrTiO_3$.

Experimental/methodology. The strontium titanate-based materials modified with Mn/Fe were synthesized by the sol-gel method. The powders with the nominal compositions: $SrTi_{0.98}Me_{0.02}O_3$, $Sr_{0.95}Ti_{0.98}Me_{0.02}O_3$, and $Sr_{0.90}Ti_{0.90}Me_{0.10}O_3$ (where Me = Fe or Mn) were obtained by the proper thermal treatment with the calcination at 900°C for 3 hours performed in the flow of air as a final step. The materials were characterized in terms of their structure (XRD analysis) and microstructure (SEM observations, the specific surface area measurements (BET), and dynamic light scattering (DLS) analysis). Additionally, to evaluate the material's redox properties temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPOx) measurements were performed. To assess the possibility of using the obtained materials in environmental catalysis the catalytic tests were performed - selective catalytic reduction of NOx with ammonia (NH_3-SCR) and selective catalytic oxidation of ammonia (NH_3-SCO) were chosen as the test reactions.

Results and discussion. The analysis of XRD results showed that all Fe-modified materials were single-phase since only strontium titanate with the cubic structure was identified. For Mn-modified materials, strontium titanate was also observed however for the samples with the highest amount of introduced manganese a small amount of additional phase - Mn_3O_4 was also observed. Nevertheless, these results clearly showed that the introduction of non-stoichiometry in the Sr-sublattice has a positive impact on the incorporation of dopant into the perovskite structure. The performed catalytical test implied that Mn-modified $SrTiO_3$-based materials have better catalytic performance compared to Fe-modified $SrTiO_3$. The conversion of NO in NH_3-SCR reaction calculated for a temperature range of 100 – 600°C for materials doped with Mn is presented in Figure 1. It should be underlined that the change of the reaction from NH_3-SCR to NH_3-SCO is clearly seen for all materials regardless of the amount of introduced dopant and the assumed Sr non-stoichiometry.

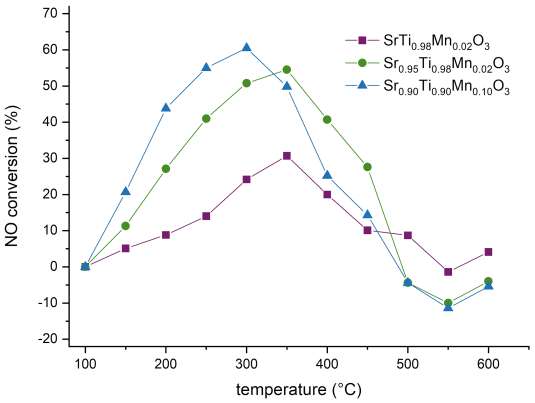

Figure 1. Conversion of NO in NH_3-SCR reaction as a function of temperature for Mn-modified $SrTiO_3$ materials.

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The cluster model for ZN catalysis: Understanding catalyst activation and deactivation pathways

Giuseppe Antinucci*, Felicia D. Cannavacciuolo, Christian Ehm, Roberta Cipullo, Vincenzo Busico

Department of Chemical Sciences, University of Naples Federico II, Naples, Italy
**giuseppe.antinucci@unina.it*

Keywords: Ziegler-Natta catalysts, DFT, activation mechanism, active sites model.

Introduction. Detailed mechanistic understanding of industrially relevant heterogeneous catalysts is rare; as a matter of fact, discovery and even optimization are mostly driven by empiricism. Ziegler-Natta catalysts (ZNCs) for the production of isotactic polypropylene are no exception in this respect. Modern ZNCs are complex multicomponent formulations.[1-3] Nanostructured $MgCl_2$ is used as support, on which a titanium compound (generally $TiCl_4$) and a Lewis base called "Internal Donor" (ID) are co-adsorbed (where ID is an organic donor such as an aromatic or aliphatic mono- or diester, or a 1,3 diether). Activation of the precatalyst is carried out by an AlR_3 species (typically $AlEt_3$), usually mixed with another organic Lewis base, generally an alkoxysilane, called "External Donor" (ED).[2,3] Among the several models that have been proposed to explain donors (and possibly Al-alkyls) effects on the active Ti sites of ZNCs, the most recent and widely accepted one is the so-called "three-site model" (Figure 1).[4] According to this model, the first coordination sphere of Ti, assumed to be in the Ti(III) oxidation state, is always octahedral and C_2-symmetric (like in crystalline $TiCl_3$)[4]; steric hindrance in the second coordination sphere, on the other hand, can vary depending on whether or not the first-neighbour surface Mg or Ti atom on either side exhibits a coordination vacancy.

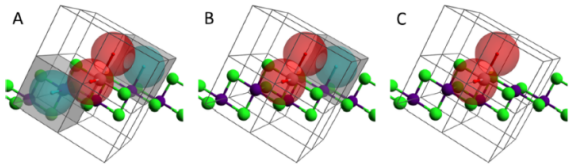

Figure 1. *Three-site model for ZN active sites.* [4,5]

Experimental/methodology. In the present work, we extended the DFT-D 'flexible-cluster' approach[6] to the computational modeling of activation and deactivation pathway in ZN catalysis. The approach offers a good compromise between speed and accuracy, and has great potential for realistic simulations of the catalytic species in industrially relevant formulations. All geometries were optmized at TPSS/cc-pVDZ level of theory, followed by a single point energy calculations at M06-2X/cc-pVTZ level.

Results and discussion. Here we provide experimental and computational evidence that $TiCl_4$ and the other components of the formulation (*i.e.*, donor and AlR_3 species) are more intimate than has been assumed so far, to the point that these systems resemble immobilized molecular catalysts more than conventional heterogeneous ones. Invoking such (metastable) species can explain some long-standing 'mysteries' regarding activation and deactivation pathways in ZN catalysis. As a matter of fact, state-of-the-art DFT-D modeling reveals how the formation of metastable $TiCl_4$-μ-AlR_3 surface species allows for low-energy activation and reduction pathways of $TiCl_4$. Similarly, direct coordination of the external donor to the Ti can explain how catalyst deactivation mechanisms, *e.g.* Cl/OR (R = Me, Et, etc.) metathesis, can occur.

Last but not least, consequences on active site models for the stereoselectivity in the chain propagation step will also be highlighted.

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Hydrosilylation/deoxygenation catalysis with “Activated borane” – a porous borane cluster polymer with Lewis acid centers

M. Lamač[1*], B. Urbán[1], M. Horáček[1], K. Škoch[2], J. Demel[2]

[1] *J. Heyrovsky Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 2155, 182 00, Prague 8, Czech Republic*

[2] *Institute of Inorganic Chemistry, Czech Academy of Sciences, Husinec-Řež 1001, 250 68, Řež, Czech Republic*

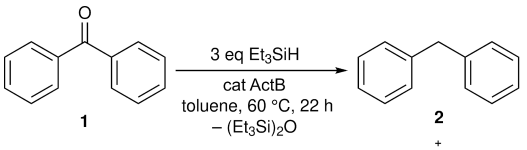
[*] *E-mail: lamac@jh-inst.cas.cz*

Keywords: Lewis acid, borane cluster, hydrosilylation, deoxygenation, heterogeneous catalysis

Introduction. Reactions catalysed by acid-based catalysts are of general importance in industrial chemistry. Heterogeneous catalysts are typically preferred based on many advantages they possess in practical applications. On the other hand, molecular borane derivatives, such as the ubiquitous $B(C_6F_5)_3$ (BCF),[1, 2] have been demonstrated to act as strong Lewis acid homogenous catalysts in many reactions, including those featuring uncommon mechanisms (e.g., Frustrated Lewis pair chemistry). Recently, “Activated borane” (**ActB**)- a solid porous amorphous polymer prepared by co-thermolysis of decaborane(14) (*nido*-$B_{10}H_{14}$) and organic hydrocarbons was reported.[3] This material emerged as a promissing candidate for heterogeneous catalysis, because it features Lewis acid centres, likely of a tricoordinated borane character, suitable for similar transformations as known for BCF.

Experimental/methodology. In this contribution we would like to present screening of catalytic properties of three different newly prepared **ActB** materials prepared from toluene, cyclohexane and *n*-hexane in hydrosilylation/deoxygenation reactions of various carbonyl substrates (ketones, aldehydes) with Et_3SiH as the reductant of choice. Testing was performed as batch reactions in various solvents and different conditions (temperature, stoichiometry, etc.) were studied. Selected reactions were tested also under flow conditions using an XCube microfluidics-based system.

Results and discussion. It has been confirmed that **ActB** materials are capable heterogeneous Lewis acid catalysts for the above type of transformation. The activity and selectivity toward different products (deoxygenation vs silylation) changes with the nature of the material and consequently with the strength of the Lewis acid centers.



catalyst	product distribution		
	1	2	3
ActB-Tol	0	>99 (88)	0
ActB-cyHx	0	>99	0
ActB-nHx	83	12	5

Acknowledgments

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Designing innovation catalyst for the synthesis of plasticizers based on hybrid material deep eutectic solvent and metal oxide

P. Latos[1*], J. Gabzdyl[1], A. Chrobok[1]

[1] *Silesian University of Technology, Gliwice, Poland*
[*] *Piotr.latos@polsl.pl*

Keywords: Deep eutectic solvent, esterification,

Introduction. Deep eutectic solvents (DESs) are an emerging class of materials promising for applications as inexpensive "designer" solvents with tunable physicochemical properties. A detailed review of the current literature reveals the lack of predictive understanding of the microscopic mechanisms that govern the structure−property relationships in this class of solvents. Metal oxide are used as substrates for the synthesis of various task-specific materials. Their phase, morphology, particle size and purity, often, are of significant importance for applications, such as catalysis, photovoltaics, and batteries. It is essential to obtain metal oxide particles with defined specific characteristics, which give control over optical and electronic properties. On the other hand the use of solid metal oxides in catalysis causes isolation problems. Metal oxide particles can be suspended in the reaction mixture and a series of unit operations are necessary to separate the catalyst. To overcome this issue metal oxide can be dissolved in DES.

Experimental/methodology. In this work, dissolution experiments were performed in the popular DES choline chloride-urea (molar ratio 1:2) by suspending the ZnO (0,8 wt%) at temperature below 100 °C in order to avoid the decomposition of urea. The driving force of dissolution is the coordination of urea to the metal atom. The amount of zinc oxide was determined by ICP-OES and XRF analysis.

Results and discussion. A hybrid system based on DES and ZnO was tested as catalyst in transesterification reaction of dimethyl terephthalate with butanol resulted in the synthesis of alternative non-phthalate plasticizer. Butyl terephthalate was obtained in high yield (92%) and full conversion dimethyl terephtalate, under mild reaction conditions at 100–120 °C and using a 10:1 molar ratio of alcohol to ester and 3.2 wt% of catalyst.

During the reaction course, the formation of the second ester phase was observed what facilitates the reaction progress, shifting the equilibrium towards the ester formation. Lower phase was consisted with catalyst and methanol and the upper phase contained product and unreacted butanol.

Another important parameter for industrial application is the stability of the catalyst and the possibility of its further reuse in following processes. To demonstrate the stability of a hybrid system based on DES and ZnO the post reaction two-phase mixture was separated and the lower phase (containing mainly catalyst) was dried using rotary evaporator and used for the next cycle. The studied catalyst was stable in ten consecutive cycles and could be used without any loss of activity.

In summary, a new catalyst for the synthesis of butyl terephthalate in the presence of hybrid system based on DES and ZnO has been developed. This work contributes to the development of sustainable and environmentally-friendly processes for the production of green plasticizers.

Acknowledgments

This work was financed by the National Science Centre, Poland (grant no. UMO-2020/39/B/ST8/00693).

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Influence of Spatial Distribution between CeO_2 and Bimetallic Nanoparticles for CO_2-Assisted Pentane Oxidative Dehydrogenation

Gayoung Lee [1,4], Muhammad Numan [1], Eunji Eom [1], Jae Won Shin [2], Michal Mazur [4]
Dae-Heung Choi [3] and Changbum Jo [1,*]

[1]*Department of Chemistry and Chemical Engineering, Inha University, Incheon, Republic of Korea*
[2]*Center for Nanomaterials and Chemical Reactions, Institute for Basic Science, Daejeon, Republic of Korea*
[3]*Petrochemicals R&D, LG Chem, Daejeon, Republic of Korea*
[4]*Department of Physical and Macromolecular Chemistry; Faculty of Science, Charles University, Hlavova 8, 128 43, Prague 2, Czech Republic*
[*] *jochangbum@inha.ac.kr (C.J.)*

Keywords: Bi-functional catalyst, Oxidative dehydrogenation, Nanoscale intimacy, CO_2, Soft oxidant

Introduction.

The use of CO_2 as a soft oxidant, in the dehydrogenation of alkane, can increase the thermodynamic yield of olefins by removal of H_2 *via* reverse water gas shift (rWGS) reaction and improve the catalyst lifetime by facilitating coke removal [1]. Classical CO_2-oxidative dehydrogenation catalysts are bi-functional, composed of (1) noble metal nanoparticles and (2) reducible metal oxide nanoparticles on a high surface area support. The metal nanoparticles are catalysts for the generation of olefins from paraffins by dehydrogenation while the reducible metal oxides activated CO_2 to facilitate the rWGS reaction. Recently, Pt_1Sn_1 intermetallic catalysts exhibited high catalytic activity during the dehydrogenation reaction [2]. We explored the combination of silica-supported Pt_1Sn_1 intermetallic nanoparticles (Pt-Sn@SiO_2) and CeO_2 as a bi-functional catalyst for C_5 oxidative dehydrogenation with CO_2 (CO_2-ODH). To prevent thermal cracking reaction, it is crucial to maintain the reaction temperature below 400 °C, where the activation of CO_2 is limited, necessitating an increase of the cerium content. However, an excess of cerium oxide can hinder the formation of intermetallic compounds between Pt and Sn, leading to significant loss of selectivity towards olefins. To address this challenge, we examined the CO_2-ODH activity concerning the intimacy between Pt-Sn alloy and CeO_2.

Experimental/methodology.

The Pt-Sn@SiO_2 catalyst was prepared using the incipient wetness impregnation method while CeO_2@SiO_2 was synthesized by the co-precipitation method. The Pt-Sn@SiO_2 and CeO_2@SiO_2 were physically mixed with the weight ratio of 1 to 1. On the other hand, co-impregnated catalyst was prepared by loading the Pt and Sn precursors onto CeO_2@SiO_2 by incipient wetness impregnation and calcined in air for 2 h at 350 °C.

Results and discussion.

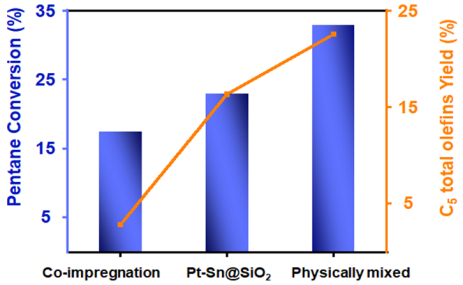

Figure 1. Pentane conversion and olefins yield obtained using different integration methods. Reaction conditions: temperature = 500 °C, molar flow ratio of CO_2:Ar:C_5 = 4:4:1, catalyst amount = 0.2 g.

For the co-impregnated catalyst, the XPS and CO-FTIR results confirmed that the strong interaction between Pt and Ce hindered the formation of Pt-Sn intermetallic nanoparticles (NPs). In contrast, for the physically mixed catalyst, Pt-Sn intermetallic NPs were not disturbed due to the nanoscale positioning of the

Pt-Sn alloy and CeO_2 sites. As a result, the physically mixed catalyst demonstrated a significantly higher olefin selectivity (68.7%) compared to the co-impregnated catalyst (20.9%). Furthermore, the presence of CeO_2@SiO_2 can facilitate the rWGS reaction, leading to an enhancement in pentane conversion (32.8%) when compared to the Pt-Sn@SiO_2 catalyst (22.9%).

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Computational design of robust catalyst beds for single-atom OER catalysts

Swetareakha Ram[1], Seung-Cheol Lee[1,2] and Satadeep Bhattacharjee[1*]*

[1]Indo Korea Science and Technology Center, Bangalore, India
[2]Electronic Materials Research Center, KIST, Seoul 136-791, South Korea
[*]s.bhattacharjee@ikst.res.in
[*]leesc@kist.re.kr

Keywords: Single Atom Catalysts, OER

Introduction. The use of single metal atoms has been considered as an efficient way to improve catalytic activity. The strategy of single-atom (SA) recombination with MXenes has been successfully applied in electrocatalyst research [1,2]. More importantly, with the development of single-atom catalysts (SAC), it is relatively easy to establish intrinsic reaction mechanisms by pointing out the nature of catalytically active sites. A strong interaction between the individual atoms and the support is the key factor for the stabilization of the SACs, affecting their electronic structures and catalytic performance. The development of a low-cost and high-efficiency catalyst for the oxygen evolution reaction (OER) is essential to meet the future industrial demand for hydrogen production through electrochemical water splitting. Most MXene surfaces with oxygen (O) end groups are reported to be more stable than the -OH and -F terminated surfaces [3]. The electron energy loss spectroscopy (EELS) experiment shows the absence of the F group on MXene [4.] Furthermore, the OH group would be converted to the O group on high-temperature annealing [5] and it is possible to synthesize O-terminated MXene in Attempt. Cobalt (Co) has emerged as an interesting base metal due to its catalytic power to split water. In this work we have focused on oxygen (O) terminated Ti and Mo-based MXenes, Ti_3CO_2, Mo_2CO_2 and $Mo_2Ti_2C_3O_2$. We systematically investigate OER performance for single Co-atom adsorbed in O-vacancy MXene surface. We find that the OER activity of the SAC can be tuned using the vacancy of the surface termination in the substrate. The charge transfer between the SAC and the substrate, in particular, can be tailored to improve catalytic activity. The magnetic moment at the SAC site is also important. We demonstrate these findings using overpotential calculations.

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Packed bed of 3D printed catalysts for CO_2 methanation

J. Lefevere[1*], B. Michielsen[1]

[1]*Flemish Institute for Technological Research - VITO, Sustainable Materials Department, Boeretang 200, 2400 Mol, Belgium*

Keywords: 3D printing, CO_2 methanation, upscaling

Introduction. 3D printing offers a wide range of opportunities for the future, although still some challenges need to be overcome before a widespread industrial implementation can happen. In the chemical industry, 3D printing can be used for producing lab ware, reactors or inert supports for catalysts. Another possibility is the direct printing of catalytic material. Several examples of 3D printed catalysts can already be found in literature [1,2], showing benefits in terms of pressure drop as well as minimizing mass transfer limitation compared to traditional shaped pellets. However, the benefits of 3D printed catalysts need to be balanced versus the extra cost of production. For industry, questions still remain concerning the quantification of these benefits, implementation of 3D printed catalyst in industrial reactors and cost of production on large scale. In this work, steps have been taken to get closer to an answer on these questions.

Experimental. 3D printed alumina structures were prepared using direct ink writing (DIW). After printing of 4 different designs, the structures were calcined and impregnated with nickel for testing in CO_2 methanation reaction. For the first time ever, a packed bed of 3D printed structures was tested and compared with catalyst pellets. Both catalytic properties as well as pressure drop of the different shapes were evaluated. Additionally, a pilot production process for 3D printed catalysts has been set-up to study the feasibility and related costs of producing 3D printed catalysts on large scale.

Results and discussion. Pressure drop measurements revealed a significantly lower pressure drop over the packed beds of 3D printed structures compared to traditional pellets. The measurements also prove that the gas flow effectively flows through the structures and not solely around them as pressure drop over the bed decreases with higher porosity in the 3D printed samples with the same dimensions. In CO_2 methanation 3D printed catalysts show increased activity at lower temperatures compared with the pellets. The upscaling efforts indicate that it is possible to produce 3D printed catalysts on a multi-ton scale. Running this equipment gives insights in the cost of production and feasibility of large-scale production of 3D printed catalysts. The key steps in the process were detected and requirements for further upscaling to industrial levels identified.

This work shows the potential of large-scale production and implementation in industrial reactors of 3D printed catalysts. This opens a new window towards further tuning of catalysts in function of desired properties. The pilot production set-up gives the information needed for the next step: full industrial scale production and an indication of cost price on case-per-case base.

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Partial hydrogenation of biofuel from Waste Cooking Oil by Steel Slags based catalyst

M. S. Leone,[1] P. Mastrorilli,[1] M. M. Dell'Anna[1]
[1]*DICATECh department of Politecnico di Bari, Bari, Italy*

[*]*mariastella.leone@poliba.it*

Keywords: Hydrogenation, FAMEs, steel slags

Introduction. Growing environmental pressure to reduce waste and contamination leads to consider recycling solutions. Wastes offer an opportunity in terms of catalysis. The growing interest in their direct application as active materials is mainly driven by a combination of economic and environmental reasons. In this context, steel slags[1] can play a significant role in catalysis because of its unique chemical composition and physical qualities. Their use is of great economic importance and could contribute to the reduction of solid waste. Herein, we report on the synthesis and characterization of a new catalyst based on steel slags with magnetic properties able to facilitate its recovery and reuse after the catalytic cycle. This new material was constituted of a nanocomposite of nickel nanoparticles and iron oxides deposited onto steel slags as support with basic features, and it was used as catalyst for the partial hydrogenation of FAMEs (Fatty Acid Methyl Esters)[2] coming from waste cooking oil. The partial hydrogenation reaction aimed at selectively converting all C18 polyunsaturated esters into C18:1 monounsaturated product, thus turning a waste into a feedstock for valuable biofuel.

Experimental/methodology.

Catalyst synthesis

$FeCl_3 \cdot 6H_2O$ (6 mmol) and of $FeSO_4$ (3 mmol) were dissolved in deionized water (130 mL) and subsequently added of steel slags (2.08 g). The mixture thus obtained was kept under stirring for 6 hours at 35°C, and then centrifuged and removed of the surnatant solution. The obtained solid was washed 3 times (5 mL) with deionized water and left overnight at 85°C to get a brown solid (2.28 g, Fe/SS). Subsequently, 0.82 g of Fe/SS were added to a solution obtained by dissolving $NiCl_2 \cdot 6H_2O$ (0.73 g) in 20 mL of deionized water.The mixture was kept under stirring at 65°C overnight, and then it was dried at 85°C for 16 hours. The obtained brown material was calcined at 300°C under dihydrogen (5 bar) for 30 minutes, turning into the final red solid employed as the catalyst (1.15 g, Fe-Ni/SS).

Catalytic run

FAMEs (125 mg) from WCO, Fe-Ni/SS (50.0 mg) and 5 mL of methanol were put in stainless steel autoclave under dihydrogen atmosphere at an initial pressure of 5 bar for 3 h at 70°C. The reaction products were characterized by GC-MS.

Results and discussion. The novel catalyst based on iron oxides/nickel nanocomposites supported onto steel slags resulted active and selective in the partial hydrogenation reaction of FAMEs obtained by WCO. In fact, after hydrogenation reaction the main component of the mixture resulted the monounsaturated C18:1 methyl ester, which represents a good compromise between oxidation stability and cold flow properties of the whole blend. In addition, the catalytic system was recyclable up to five subsequent runs without losing its activity and selectivity. Further analyses are still in progress to better characterize the new synthetized material.

Acknowledgments

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Pinning of transition metal nanoparticles onto silanol-rich 2D zeolitic materials

Ang Li, Daniel N. Rainer, Martin Kubů, Jiři Čejka, and Michal Mazur

Department of Physical and Macromolecular Chemistry, Charles University, Hlavova 8, 128 43 Prague 2, Czech Republic

Keywords: Zeolites; Transition Metal nanoparticles; metal-zeolite nanocomposites; metal-silanol interactions; sintering resistance.

Introduction.

Transition metal-zeolite composites have emerged as catalysts for various industrial and laboratory-scale processes, such as hydrogenations. [1] Nevertheless, efficient synthesis of metal-zeolite composites with anti-sintering, thermally stable metal nanoparticles and reducible metal oxide nanoparticles still remains a challenge. Encapsulating of the metal species into zeolite frameworks can improve the stability of metal by the spatial confinement effect. Significant advancements in the fabrication of well-defined metal species confined within zeolites opened routes for preparation of variety of potential catalysts. Yet, it is still challenging to effectively confine some of the transition metals or reducible metal oxide nanoparticles into zeolites because of the inherent nature of these species, high surface energies with various valences, low melting points, and sensitivity at acidic and base conditions.

Recently, we have successfully encapsulated Rh nanoparticle into non-porous layered zeolitic precursor, IPC-1P. [2] The zeolitic layers have a defined silanol nests with quadruple geometry. This generates the pinning effect between the Rh species and silanol nests. Final materials show excellent sintering resistance of reducible metal oxide nanoparticles even at harsh conditions (750 °C for 6 h). Herein, we show the effective incorporation of various transition metals (Ag, Zn, Co, and Cu) into the silanol-rich layered zeolite support. Resulting materials were composites of reducible metal oxide nanoparticles supported and stabilized by zeolite.

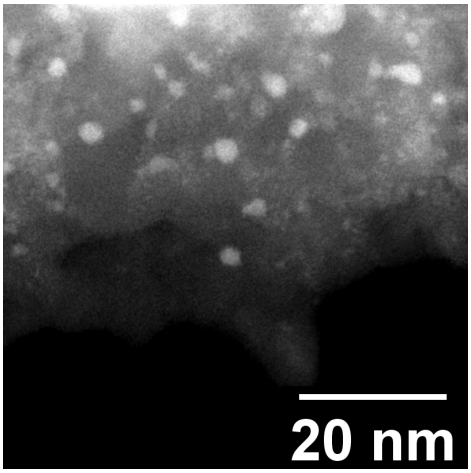

Figure 1. *Representative ADF-STEM image of Zn@IPC layered material after calcination.*

Experimental/methodology.

Silanol-rich zeolitic support with transition metal oxide nanoparticles (denoted as metal@IPCs) were prepared by introduction of metal precursors during a swelling process of IPC-1P. Layered IPC-1P was synthesized by the hydrolysis of UTL germanosilicate. Swelling of layered precursor was performed by introduction of a long surfactant (docosyltrimethylammonium hydroxide) into the interlayer space. Transition metal precursors were stabilized with protective ligands and then encapsulated simultaneously with the swelling. The final metal@IPCs were obtained after a calcination at 550 °C in air.

Results and discussion.

The produced metal@IPCs composite catalysts were investigated by PXRD, sorption of Ar, SEM, STEM, and STEM-EDS. PXRD and Ar sorption results confirmed the disorder stacking of the zeolitic layers. ADF-STEM images of calcined materials (e.g. Zn@IPC, Fig. 1.) showed that the transition metal oxide nanoparticles

were uniformly dispersed on the zeolite support. This shows the efficient stabilization of reducible metal oxide nanoparticles. Materials have shown the stability over thermal treatment, including in-situ heating in electron microscope. STEM imaging of in-situ heated materials shown the sintering behavior of the metal species at elevated temperatures.

Acknowledgments
Authors acknowledge support of the Czech Science Foundation for the project ExPro (19-27551X).

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Descriptors for hydrodeoxygenation reaction over Mo_2C catalyst

R. Meena[1,2], H. Bitter[1], H. Zuilhof[2], G. Li[1,2*]

[1]*Biobased Chemistry and Technology, Department of Agrotechnology and Food Sciences, Wageningen University and Research, PO Box 17, 6700 AA Wageningen, The Netherlands*
[2]*Laboratory of Organic Chemistry, Department of Agrotechnology and Food Sciences, Wageningen University and Research, PO Box 17, 6700 AA Wageningen, The Netherlands*
[*]*Corresponding Author's E-mail address: guanna.li@wur.nl*

Introduction. Platinum group metals (PGMs) are known for catalysing a wide range of chemical reactions involved in biomass conversion with high activity and selectivity. However, PGMs are scarce, expensive, and are susceptible to deactivation by the impurities present in the reaction systems [1]. Therefore, focus has been shifted on finding viable alternatives such as Mo_2C and W_2C transition metal carbides (TMC) [2]. While catalytic activity of TMC is to some degree known, it is still not clear what the structure-activity relationships are. In this work, we used an efficient descriptor-based approach [3] to gain insights into structure-activity relationships for Mo_2C catalyst, and then further tuned the activity of Mo_2C by heteroatom doping.

Experimental/methodology. All the DFT calculations were performed using VASP package. Electron-ion interactions were described using PAW method and PW basis set. Microkinetic modelling (MKM) was performed using MKMCXX package. The most stable β-Mo_2C (101) facet for hydrodeoxygenation (HDO) of butyric acid was chosen as a prototype for investigation of the structure-activity relationships.

Results and discussion. First, the full HDO reaction pathway over β-Mo_2C (101) surface was identified by DFT mechanistic study, Fig.1 (A). Subsequently, microscopic parameters (elementary steps and activation barriers) obtained using DFT were plugged into an MKM model to derive experimentally measurable macroscopic parameters such as surface coverages and degree of rate control (DRC) coefficients. DRC analysis (Fig.1 (B)) shows that butanol dissociation is the rate-determining step. To facilitate this reaction step, we doped the metal active site with a range of transition metals (*M*), as in Fig.1 (C). Upon electronic structure analysis, Fig.1 (D), we discovered that *M* (*d*-band filling) and *M* (radius) are decent descriptors correlating the activity of β-Mo_2C (101) surface and doping active metal site with **Zr** *and* **Nb** can remarkably improve butanol dissociation and thereof enhance the overall activity. These fundamental understandings provide a practical strategy for tailor-made TMCs development towards HDO reactions.

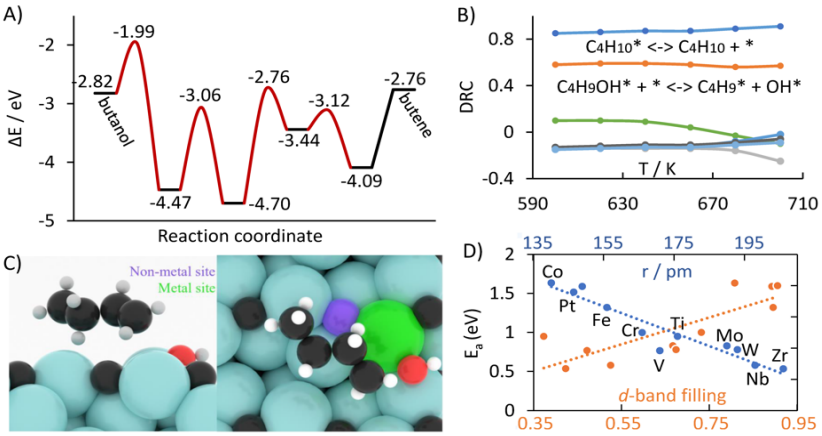

Figure 1: Descriptor screening based on mechanism and scaling relationships for HDO of butyric acid on Mo_2C catalyst.

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Influence of active-site proximity in zeolites on Brønsted-acid catalyzed reactions at the microscopic and mesoscopic levels

Teng Li, Sang-Ho Chung, Stefan Nastase, Adrian Galilea, Yan Wang, Ildar Mukhambetov, Moussa Zaarour, Juan Carlos Navarro de Miguel, Jurjen Cazemier, Abhay Dokania, Liliana Panarone, Jorge Gascon, Luigi Cavallo and Javier Ruiz-Martínez*

King Abdullah University of Science and Technology, KAUST Catalysis Center (KCC), Thuwal, Saudi Arabia

javier.ruizmartinez@kaust.edu.sa

Keywords: zeolite, aluminum distribution, paired acid sites, isolated acid sites, Al-zoning, hollow zeolite, methanol-to-aromatics (MTA)

Introduction. Zeolites are the catalytic workhorses of various relevant reactions, primarily because of their acidic properties. There is general agreement that modulating the organization of aluminum and its associated acid site can further exploit the potential of zeolites [1,2]. However, to date, there have been few studies on unravelling the influence of Al distribution on acid-catalyzed reactions at the mesoscopic and microscopic levels.

Experimental/methodology. HZSM-5 zeolites with different Al distribution, i.e., intraparticle distribution and Al proximity at the nanoscale, were prepared first and characterized in detail (**Figure**). The catalysts were then evaluated in methanol-to-aromatics and olefins-to-aromatics reactions. Both static and Molecular Dynamics calculations were performed to disclouse the mechanisms [3].

Results and discussion. Our results demonstrate that Al enrichment at positions closer to the external surface results in more paired acid sites that exhibit enhanced activity than the isolated ones. As suggested by theoretical calculation, paired acid sites promote proceedings of hydride-transfer, oligomerization and cyclization reactions because of their higher protonation ability and enhanced stabilization effect. Secondly, such Al organization accelerates progression of cascade reactions to yield aromatics and alleviate their diffusion out. Exploiting the Al-zoning feature, we further fabricated hollow zeolites by desilication. Combining the optimized active sites with the improved diffusion and void-confinement properties of hollow crystals results in the highest capacity to produce aromatics (19.4 g_{carbon} $g_{zeolite}^{-1}$).

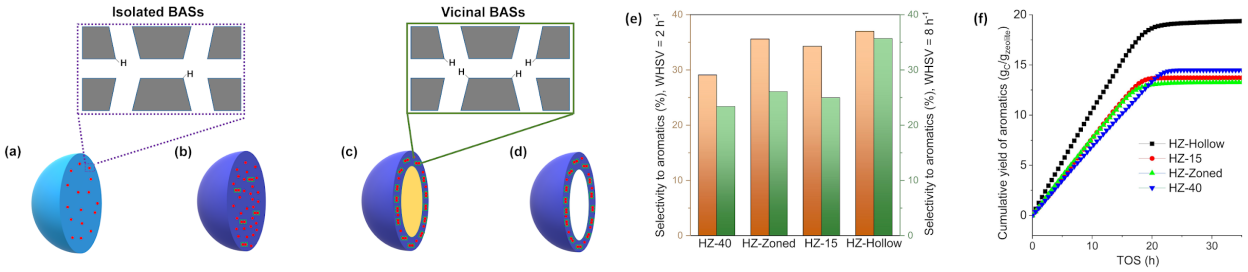

Figure. Schematic representation of the HZSM-5 catalysts used for comparsion and their catalytic performance at 400 °C. (a) HZ-40 (Si/Al=40, homogeneous Al distirbution). (b) HZ-15 (Si/Al=15, homogeneous Al distribution). (c) HZ-Zoned (Si/Al=40, Al-zoned). (d) HZ-Hollow (Si/Al=18, hollow zeolite). (e) The averaged selectivity to aromatics over 5 h time-on-stream at WHSV = 2 h^{-1} and WHSV = 8 h^{-1}. (f) Cumulative yield of aromatics with TOS over different zeolite samples at WHSV = 8 h^{-1}. BASs: Brønsted acid sites. WHSV: weight hourly space velocity of methanol.

Acknowledgments

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Cluster-sized alloys on zeolite for robust ethylene removal at 0 °C

Mingyue Lin[1], Haifeng Wang[2], Tamao Ishida[2], Guangli Xiu[1*], Toru Murayama[2*]

[1]*East China University of Science and Technology, Shanghai, P.R. China*
[2]*Tokyo Metropolitan University, Tokyo, Japan*
[*]*Corresponding Author's E-mail address: murayama@tmu.ac.jp, xiugl@ecust.edu.cn*

Keywords: Ethylene removal, cluster-sized alloys, acetate intermediate, stability

Introduction. Fruits and vegetables and other edible agricultural products will continuously release ethylene gas as the ripening agent, which will accelerate the food aging and quality deterioration even in the cold chain transportation and storage. Catalytic oxidation has widely been considered as a desirable method for efficient removal of trace ethylene at low temperatures. However, all current reported catalysts are prone to poisoning and deactivation at around 0 °C, and the continuous operation time for ethylene removal is less than 2 hours[1,2], which is difficult to meet the requirements of long-time food preservation. Solving the poor catalyst stability is the key.

Experimental/methodology. Au-Pt alloy NPs/ZHM20 catalysts with different molar ratios of Au and Pt were prepared by sol immobilization method[3]. Physical and chemical properties were characterized by ICP-AES, HAADF-STEM, EDS, XANES, XRD, XPS, etc. C_2H_4 removal measurements were performed on a fixed-bed flow with U-shaped glass reactor. The catalyst was pretreated at 150 °C for 2 h under N_2 flow (50 mL min^{-1}) before the test. Reactant gas that contained 50 ppm C_2H_4/20% O_2/N_2 balance was fed to the catalyst bed with a total flow rate of 10 mL min^{-1}, and the inlet and outlet concentrations of C_2H_4 and CO_2 were measured by an online 490 Micro GC system (Agilent). The space velocity was 3000 mL h^{-1} g^{-1}.

Results and discussion. We prepared gold-platinum (Au-Pt) alloy nanoparticles (NPs) catalysts ($Au_{54}Pt_{46}$/ZHM20) that showed robust C_2H_4 (of 50 ppm) removal capacity at 0 °C for 15 days (360 h) and that the performance of the used catalysts would be fully recovered by heat treatment for at least two times. This catalyst showed two stages of C_2H_4 removal: the first stage was attributed to the adsorption of C_2H_4 and the second could be due to the catalytic conversion of C_2H_4 to intermediates on $Au_{54}Pt_{46}$/ZHM20. Investigations by *in-situ* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy of C_2H_4 oxidation and online temperature programed desorption measurements of the spent catalyst suggested that the Au-Pt nanoalloys favor the formation of acetic acid (AcOH) from selective ethylene oxidation. And this on-site-formed acetate intermediate would partially cover the catalyst surface at 0 °C, thus exposing active sites to prolong the continuous and effective C_2H_4 removal .

Acknowledgments

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Structural and morphology studies of nanocomposites ZnO-$ZnAl_2O_4$ obtained by hydrothermal carbonization and thermal treatment

K. Antoniak-Jurak*, A. Mrozek, R. Bicki, P. Kowalik

Łukasiewicz Research Network – New Chemical Syntheses Institute, Pulawy, Poland
**katarzyna.antoniak@ins.lukasiewicz.gov.pl*

Keywords: hydrothermal carbonation raw ZnO and AlOOH, crystallization, morphology transformation, nonocomposites ZnO-$ZnAl_2O_4$

Introduction.
The combination of ZnO and aluminas to construct the ZnO-$ZnAl_2O_4$ nanocomposites are used in a number of applications as sensors, high temperature ceramic material, photocatalysts, supports and catalysts for various chemical reactions [1]. These materials show a number of unique surface properties providing high reactivity [2]. The present study examined the effect of different parameters of CO_2 saturation of raw ZnO and boehmite (AlOOH) in aqueous suspension on changes in morphology and structure of hydroxy-carbonate precursors and final oxide systems derivatives. The CO_2 saturation kinetics of aqueous ZnO-AlOOH suspensions are discussed. Moreover, the studies of the changes of morphology and structure of ZnO-$ZnAl_2O_4$ were also presented.

Experimental.
The preparation of ZnO-$ZnAl_2O_4$ (with a Zn/Al molar ratio of 0.7) was carried out by hydrothermal carbonation of a suspension of raw ZnO (ZnO pure, 99.5%wt., POCH) and boehmite (AlOOH, Versal-250) in a policlave lab pressure reactor (BÜCHI). The effects of temperature (ranging from 15 to 60 ^oC), suspension concentration, pressure (up to 5 bar) on the kinetics of the process as well as on changes in morphology and phase composition were studied. The hydroxycarbonates obtained were subjected to subsequent thermal treatment (in the temperature range of 500-900 ^oC). The materials after saturation were investigated by XRD, SEM, TG/DTG coupled with MS methods and their calcination products (ZnO-$ZnAl_2O_4$ nanocomposites) were additionally subjected to TPD_CO_2 and TPD_NH_3 studies. HR-TEM studies were also performed for selected samples.

Results and discussion.
It has been shown that irrespective of the concentration of the ZnO-AlOOH suspension, the conversion of ZnO to carbonate forms proceeds at a relatively high rate during the initial phase of carbonation, while in the later stages the process proceeds constantly at a significantly lower rate. The temperature is a factor that slows down the rate of ZnO to $ZnCO_3$ conversion which when taking into account Arhenius' law, shows that the carbonation reaction is not a limiting step. The rate of conversion of ZnO to $ZnCO_3$ is limited by the rate of dissolution of ZnO and/or the concentration of CO_2 in the reaction medium (CO_2 solubility in water decreases with temperature increase). A strong influence of hydrothermal carbonation parameters, especially temperature and pressure, was shown to have altered the surface morphology and phase composition of the carbonate precursors. As temperature and pressure increase, the carbonation products show a radically different phase composition. It was found that the calcination conditions of Zn-Al hydroxy-carbonate precursors strongly determine the surface-structural, acid-base properties and surface morpho-logy of ZnO-$ZnAl_2O_4$ nanocomposites.

Acknowledgments
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Multiple doping of perovskite oxide catalysts – Unravelling the complex exsolution behavior

L. Lindenthal[1,2], H. Drexler[1,2], J. Rollenitz[1,2], F. Schrenk[1,2], T. Rocha[3], T. Mori[3], L. Borges[3], C. Rameshan[1,2*]

[1]*Montanuniversität Leoben, Chair of Physical Chemistry, Leoben, Austria*
[2]*Technische Universität Wien, Institute of Materials Chemistry, Vienna, Austria*
[3]*Center for Research in Energy and Materials (CNPEM), LNLS, Campinas, São Paulo, Brazil*
[*]*christoph.rameshan@unileoben.ac.at*

Keywords: perovskite oxides, exsolution, nanoparticles, *in-situ* studies

Introduction. Exsolution from perovskite oxide catalysts has drawn increasing interest in the last decade. In this process, catalytically active metal nanoparticles decorating the material's surface are formed by selectively reducing metal elements within the perovskite structure, which consequently migrate to the surface [1]. Many recent studies are focusing on systems with one or two reducible elements [2]. In the latter case, often formation of alloyed particles has been observed. In this work, the perovskite NCF ($Nd_{0.6}Ca_{0.4}FeO_{3-\delta}$) has been doped with a combination of Co, Cu and/or Ni. Thus, up to three reducible elements (including the host metal Fe) are present, leading to even more complex exsolution behavior, as all of them can contribute to the resulting nanoparticle composition.

Experimental/methodology. Several single or dually doped variations of NCF have been synthesized and characterized utilizing a combination of complementary techniques. In particular, the reduction behavior – accompanied by exsolution – has been investigated, as well as the chemical composition and morphology of exsolved nanoparticles. Methods used include Temperature Programmed Reduction (TPR), (*in-situ*) X-Ray Diffraction (XRD), X-Ray Absorption Spectroscopy (XAS), and Scanning Electron Microscopy (SEM).

Results and discussion. Choosing the doping element(s) in combination with control of the reduction parameters (gas phase, temperature, time, etc.) opens up a variety of resulting surface morphologies. Depending on the exact conditions, it is possible to have a mixture of particles with different metallic phases (eg. Ni doping leads to Ni-rich fcc particles and Fe-rich bcc particles), or homogeneous particles with an alloy phase (eg. a FeCoCu alloy in the case of combined Co- and Cu-doping, cf. Figure 1).
These insights allow precise tuning of the material's surface for an intended application. For example, in catalysis particles with optimized catalytic activity can be achieved.

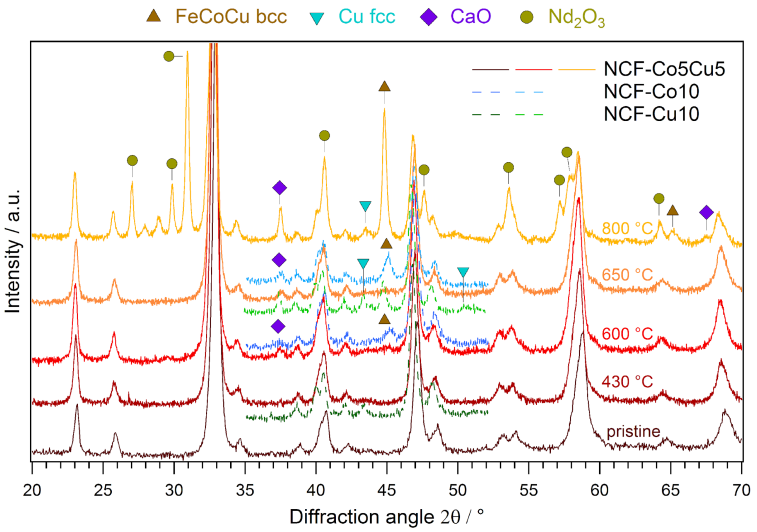

Figure SEQ Figure * ARABIC 1: XRD patterns of Co- and/or Cu-doped NCF after reduction at various temperatures, revealing exsolved phases.

Acknowledgments
This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement n° 755744 / ERC - Starting Grant TUCAS).

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Influence of the starting biomass in the Pd-biochar catalyst properties

L. Longo*[1], M. Signoretto[1], F. Menegazzo[1], A. Di Michele[2]

[1]*Ca' Foscari University, Venezia, Italy*
[2]*University of Perugia, Perugia, Italy*
[*]*lilia.longo@unive.it*

Keywords: biochar, biomass, Pd catalyst, hydrogenation.

Introduction.

The transformation and use of biomass are fundamental steps for the circular economy transition. From the pyrolytic decomposition of biomass, it is possible to obtain three different fractions. The gas fraction can be treated to obtain syngas, the liquid fraction, bio-oil, is a source of chemicals and biofuels. The solid fraction, namely biochar, is mainly considered a byproduct of the production of bio-oil and biogas, however it is a sustainable material able to immobilize organic carbon in its structure, reducing the greenhouse effect. Biochar can be obtained by all type of biomass and in particular from wastes [1]. The thermal treatments and the activation can tune the morphology, porosity, and surface functionalization of the material, to adapt it to the desired scope. It can be employed as support for metal nanoparticles dispersion, used in different catalytic fields, such as contaminant degradation, synthesis of fine chemicals, hydrogenation/oxygenation reactions [2], reforming etc. In this work, four different types of biomasses were considered, due to their different nature and composition: a) hazelnut shells (HS), a lignocellulosic biomass b) broken rice grains (BR), mainly made of starch, c) rice husks (RH), a lignocellulosic biomass with a high amount of silica (30 wt.%) and c) chromium free leather tannery waste (L), a byproduct of the tannery industry, made of collagen and tanning agents. The biochars were characterized, activated, and employed as support for Pd NPs. The catalytic activity was evaluated in a model reaction, such as benzaldehyde hydrogenation, and the characteristic of the catalysts were related to the biochar features.

Experimental/methodology.

Biomasses were subjected to slow pyrolysis at 700°C and the obtained biochars were further activated by steam at 850°C. The activated biochars were washed by HCl 1M to eliminate residual ashes and then 0,6 wt.% of Pd was dispersed on the support by wetness impregnation method, and reduced by sodium formate at 80°C. All the materials were fully characterized by several techinques, such as CHNS elemental analysis, FT-IR, N_2 physisorption, Temperature Programmed Reduction, SEM, TEM, XRD etc. The catalysts were compared in the hydrogenation of benzaldehyde, performed at room temperature and atmospheric H_2 pressure, in ethanol as solvent.

Results and discussion.

The catalysts obtained showed different performances, that were related to the nature of the support. Pd on Activated Rice Husk biochar (Pd/ARH) showed the best results, followed by Pd/AHS. At very mild conditions, Pd/ARH was able to convert benzaldehyde to benzyl alcohol (82%) in 40 minutes, and to toluene (97%) in 200 minutes. On the other hand, ABR and AL showed lower activity of the final catalysts. Several was the reason were attributed to a better performance of ARH overall. Indeed, the starting biomass played a crucial role: the presence of lignin in the biomass was found to be crucial to obtain a hierarchical porous structure with micro and mesopores and inner channels both in ARH and AHS. Moreover, ARH showed a high oxygenated surface, and a hybrid organic/inorganic structure, and therefore it was able to better anchor Pd NPs on the surface and ensure a high dispersion of the metal, with a medium particle size of 3,8 nm.

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Pd-Fe catalysts boosting effect for the Selective Oxidation of Benzyl alcohol through in situ H_2O_2 production

A. Lopez-Martin*, Richard J. Lewis, Graham J. Hutchings

School of Chemistry, Cardiff University, Cardiff CF10 3AT, United Kingdom
**lopez-martina@cardiff.ac.uk*

Keywords: Alcohol oxidation, green chemistry, hydrogen peroxide.

Introduction.

Selective oxidation of benzyl alcohol to benzaldehyde is critical for laboratory and commercial processes. The low atom inefficiency of the current process and the large amounts of undesirable byproducts generated by it have pointed out the importance of the use of molecular oxygen or H_2O_2 as oxidants.[1] A group of bimetallic Pd-based catalysts has been studied in this work, with interesting results in the case of $PdFe/TiO_2$ presenting a high selectivity to benzaldehyde via the in situ production of H_2O_2 under low-temperature reactions conditions.[2]

Experimental/methodology.

Mono and bimetallic catalysts were prepared by an excess chloride impregnation procedure. The catalytic study covered the direct synthesis of H_2O_2, the degradation of H_2O_2, and the benzyl alcohol oxidation via in situ production of H_2O_2 at low temperature. Catalysts were characterized by TEM, EDX, XPS, BET and EPR experiments were also performed.

Results and discussion.

Previous studies showed that the gold incorporation into Pd catalysts had a positive effect on the production of H_2O_2 and the production of benzaldehyde.[3] The new series of catalysts were tested finding that $PdFe/TiO_2$ showed a small enhancement in the H_2O_2 synthesis, linked with a very low degradation of it. Regarding the benzyl alcohol oxidation reaction via in situ production of H_2O_2, the incorporation of Fe into the catalyst showed an incredible improvement, with productivity greater than that observed for Pd/TiO_2 and $PdAu/TiO_2$ (Figure 1).

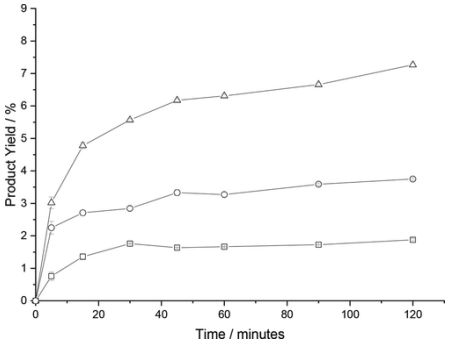

Figure 1. Catalytic activity toward the selective oxidation of benzyl alcohol as a function of reaction time. Key: 1%Pd/TiO_2 (squares), 1% $PdAu/TiO_2$ (circles), 1% $PdFe/TiO_2$ (triangles).[2]

The XPS results after reducing the samples showed a high proportion of Pd^{2+} in the case of the $PdFe/TiO_2$ catalyst, being maintained longer than the rest of the catalysts. This is in agreement with previous studies that showed how the Pd^0-Pd^{2+} domains have higher catalytic activity for both the synthesis of H_2O_2 and the selective oxidation of benzyl alcohol,[4] indicating some of the reasons for the higher activity of the 1%$PdFe/TiO_2$ catalyst at the presence of Pd^0-Pd^{2+} domains and the continual low-level production of H_2O_2 over extended reaction times.

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High performance tunable catalysts prepared by 3D printing

C. Chaparro-Garnica[1], E. Bailón-García[1], A. Davó-Quiñonero[1], P. Da Costa[2], A. Bueno-López[1], D. Lozano-Castelló[1*]

[1]*Inorganic Chemistry Department, University of Alicante, Alicante, Spain*
[2]*Institut Jean Le Rond d'Alembert, Sorbonne University, Saint Cyr L'Ecole, France*
[*]*d.lozano@ua.es*

Keywords: 3D printing, CO_2 methanation, CO-PROX, ceria-based catalysts, monolith supports

Introduction. A new method to synthesize integral carbon monoliths with a controlled channel morphology was developed in this work by combining 3D-printing technology and sol-gel polymerization. Robust and consistent carbon monoliths were obtained with a perfect replica of the channel architecture

Experimental/methodology. As a proof of concept, carbon monoliths with tortuous channels that split and join successively along the monolith length were designed. The carbon monoliths were synthesized by polymerization of a mixture of resorcinol (R), formaldehyde (F) and water (W) following a modified Pekalas's method [1] followed by carbonisation. Different R/W molar ratios (1/13, 1/15 or 1/17)were used in order to control the porosity of the resulting carbon gels. The obtained monoliths were tested as catalyst supports for the preferential oxidation of CO in the presence of H_2 (CO-PROX) [2] and in carbon dioxide hydrogenation to methane [3] after loading Cu/CeO_2 and Ni/CeO_2 active phases, respectively.

Results and discussion. The behavior of this novel carbon monolith catalyst outperforms the catalyst with a conventional honeycomb design in the tested reactions. Results show that the macroporosity of the carbon network favours the anchoring and dispersion of the active phase both in the channel surface and the carbon network. The channel architecture affects the gas diffusion both through the channel and the carbon network and in consequence, affects the active phase accessibility and activity. In CO_2 methanation (Fig. 2), the reaction rate was enhanced by 25% at 300 °C, which is attributed to an increased turbulent flow in the channel network of the advanced designs.

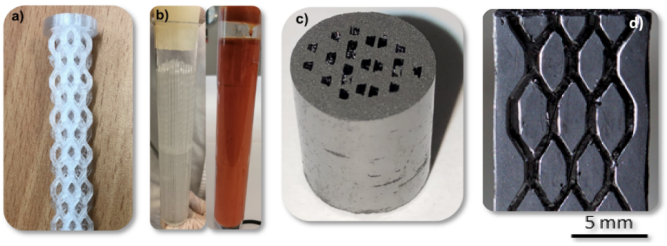

Figure 1. (a) 3D template, (b) RF formaldehyde mixture into glass tube before and after polymerization. (c) top view and (d) cross section of the obtained carbon monolith.

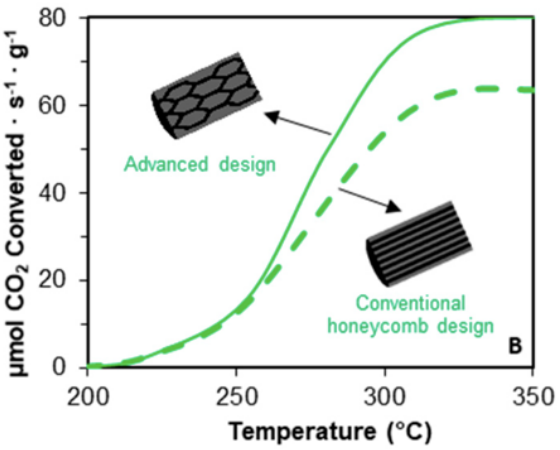

Figure 2. CO_2 methanation activity results of Ni/CeO_2 /carbon monoliths prepared in this work through 3D printing.

Acknowledgments. *Spanish Ministry of Science and Innovation (PID2019-105960RB-C22, RYC2021-034791-I, TED2021-129216B-I00, PDC2022-133839-C22) and Generalitat Valenciana, Spain (CIPROM/2021/74, MFA/2022/036).*

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Atomic Cu-N-P-C Active Complex with Integrated Oxidation and Chlorination for Improved Ethylene Oxychlorination

Hongfei Ma*, Wei Zhang, De Chen

Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, (Norway)

*Presenting author, hongfei.ma@ntnu.no

Introduction. Fine constructing the chemical environment of the central metal is vital in developing efficient single-atom catalysts (SACs). Herein, the atomically dispersed Cu on the N-doped carbon is modulated by introducing Cu−P moiety to Cu-N-C SAC. Through fine-tuning with another heteroatom P, the Cu SAC shows the superior performance of ethylene oxychlorination. The Cu site activity of Cu-NPC is four times higher than the P-free Cu-NC catalyst. And 25 times higher than the Ce-promoted $CuCl_2/Al_2O_3$ catalyst in the long-term test (>200 h). The EDC selectivity can be splendidly kept at ~99%. Combined experimental and simulation studies provide a theoretical framework for the coordination of Cu, N, P in the complex active center and its role in effectively catalyzing ethylene oxychlorination. It integrates the oxidation and chlorination reactions with superior catalytic performance and unrivaled ability of corrosive-HCl resistance. The concept of fine constructing with another heteroatom is anticipated to provide us inspiration for rational catalyst design and expand the applications of carbon-based SACs in heterogeneous catalysis.

Experimental/methodology. The Cu single atom catalyst, co-doped with nitrogen and phosphorus, was prepared by an impregnation and pyrolysis method. Lignin (purchased from St1 Renewable Energy) was used as the carbon source and support.

Results and discussion. The Cu-NPC catalyst shows high activity and selectivity during the 200 hours on stream with the EDC selectivity of ~99%. It is affording a 4-times conversion than that of the Cu-NC catalyst. The production rate of Cu-NPC is much higher (~25 times) than the Ce-doped $CuCl_2/Al_2O_3$ catalyst, as shown in Figure 1b. Such a high intrinsic site activity made the catalyst highly active so that the production rate per catalyst mass was also higher compared to the $CeCu/Al_2O_3$ catalyst (~1.2 times), as shown in Figure 1b. However, the Cu-NC shows a much lower activity per gram catalyst compared to the $CeCuCl_2/Al_2O_3$ catalyst, but a much higher activity in terms of the Cu amount. Herein, doping P into the Cu-NC can greatly enhance the reactivity, in terms of per unit gram of catalyst and per unit amount of Cu. The results demonstrated that the Cu-NPC is more active, selective, and stable for ethylene oxychlorination compared to the Ce-doped $CuCl_2/Al_2O_3$-based catalysts.

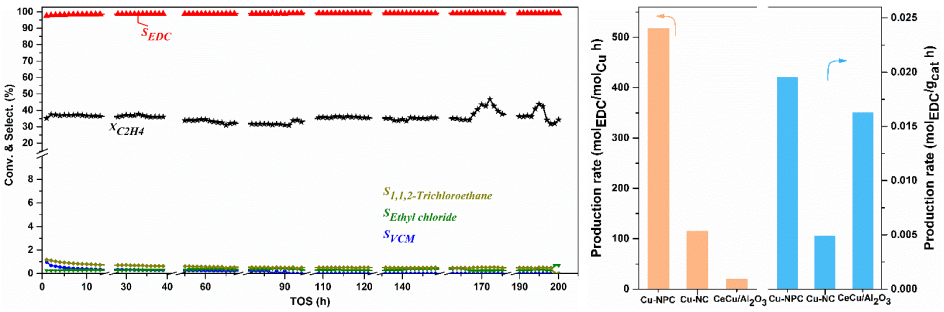

Figure 1. (a) C_2H_4 conversion and product selectivity of Cu-NPC catalyst, (b) Comparison of the production rates (calculated from the reaction at the 3rd hour).

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Progress on the Implementation of More Sustainable Hydroformylation by Supported Liquid Phase (SLP) Catalysis

M. Madani[1], L. Schill[1], N. Zahrtmann[2], R. Portela[3], L. Arsenjuk[4], R. Franke[4], R. Fehrmann[1], A. Riisager[1*]

[1]Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, 2800 Kgs, Lyngby, Denmark; [2]LiqTech Ceramics A/S, 2750 Ballerup, Denmark; [3]Institute of Catalysis and Petrochemistry (ICP-CSIC), Spectroscopy and Industrial Catalysis Group, Madrid, Spain; [4]Evonik Operations GmbH, D-45772 Marl, Germany.

[*]ar@kemi.dtu.dk

Introduction. Supported liquid-phase (SLP) catalysis is an industrially relevant approach to heterogenize homogeneous catalysts by immobilizing a liquid phase containing the catalyst complexes on the inner surface area of porous support material [1] (Figure 1). The MACBETH (Membranes And Catalysts Beyond Economic and Technological Hurdles) consortium is working towards applying a breakthrough technology consisting of a SLP catalyst with in-situ product separation in a catalytic membrane reactor (CMR) to the gas phase hydroformylation (HyFo) of C_4 olefins to yield n-pentanal [2]. This encompases optimization of the support material, the liquid-phase composition and the membrane which minimizes unwanted aldol formation by in-situ aldehyde removal. Upscaling aspects including construction of a pilot plant (TRL 7), solvent selection for in-situ liquid-phase addition and precious metal recovery are also in focus.

Experimental/methodology. Macroporous monoliths made of sintered α-SiC powder were wahscoated (1 or 2 times) with nanometer-sized silica particles (7 and 70 nm) [2] to add mesopores of various sizes and volumes for catalytic phase retention. Afterwards, SLP catalysts were obtained by impregnating the monoliths with a Rh-bpp-sebacate catalyst system (Rh/bpp/sebacate = 1/4/16 molar ratio) and tested for 1-butene HyFo at 120 °C and 10 bar (1-butene:CO:H_2 = 1.04:4.46:4.46 mmol/min).

Results and discussion. The SLP systems demonstrated stable performance for 140 h time on stream with low aldol formation. The supports containing 70 nm silica nanoparticles (NPs) exhibited higher activity but also slighlty lower regioselecitvity towards the desired linear product (Figure 2). Causes of the performance differences were investigated and further optimized, e.g. pore filling degree and liquid phase composition. Progress pertaining other building blocks such as, e.g. the membrane as well as the the crucial interplay of components will also be presented.

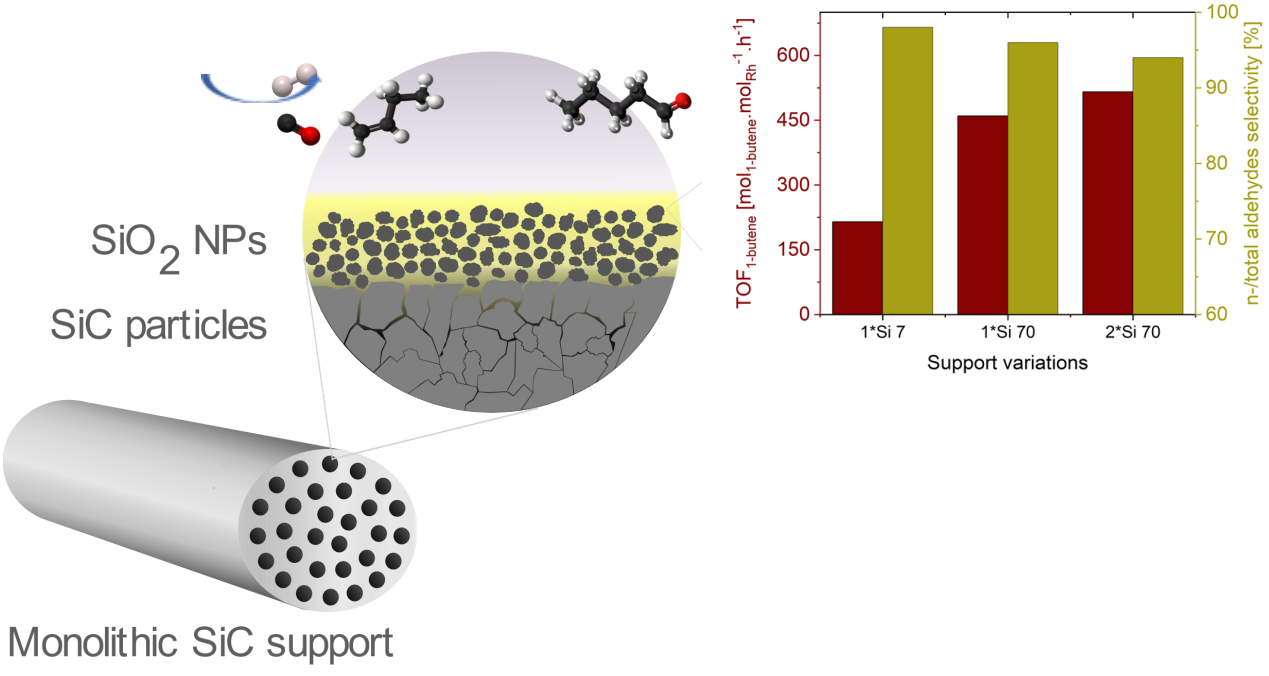

Figure 1: Monolithic SLP catalyst containing SiO_2 NPs

Figure 2: Activity and regioselectivity in the HyFo of 1-butene over SLP catalysts with various silica washcoats

Acknowledgments

The authors gratefully acknowledge financial support from the European Commission within the Horizon2020-SPIRE project MACBETH under grant agreement N°869896.

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Rational Solvent Selection for the Preparation of Industrial Monolithic-Supported Liquid Phase (SLP) Olefin Hydroformylation Catalyst

M. Madani[1], L. Schill[1], L. Arsenjuk[2], R. Franke[2], R. Fehrmann[1], A. Riisager[1*]

[1]Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, 2800 Kgs, Lyngby, Denmark; [2]Evonik Operations GmbH, D-45772 Marl, Germany.
[*]ar@kemi.dtu.dk

Introduction. Supported liquid-phase (SLP) catalysis has successfully been established as an industrially attractive approach to heterogenize homogeneous catalysts [1]. Monolithic SLP systems have recently shown great potential in gas-phase hydroformylation (HyFo) of C_4 olefins to yield n-pentanal [2] and the MACBETH consortium [3] is on the verge of larger scale deployment at industrial site (TRL 7). This entails in-situ impregnation of support materials with a catalyst stock solution containing the SLP components (Table 1) under inert conditions. Dichloromethane (DCM), which was used for lab scale studies, is not an viable option for upscaling due to EHS concerns. Here, an in silico solvent selection has been performed and promising solvent candidates validated experimentally against DCM.

Experimental/methodology. A rational solvent pre-screening on over 5000 compounds was performed employing the following criteria: (i) boiling points, (ii) COSMO based activity coefficients, (iii) QSAR based carcinogenicity and mutagenicity predictions. The shortlisted solvents were checked for, e.g. toxicity and pyrogenicity and cost estimates served as the last filter. The solubilites of bpp and sebacate were measured experimentally in the most promising solvents and benchmarked against DCM. Gas-phase HyFo of 1-butene was performed for SLP catalysts impregnated with DCM and methyl tert-butyl ether (MTBE).

Results and discussion. The final list of solvent candidates was heavily dominated by esters and ethers, including MTBE - an economic and widely available DCM replacement. Solubilities of bpp in MTBE, dimethoxymethane and methylpropionate were measured to be 18.0, 20.6 and 24.5 g/L, respectively. The corresponding sebacate solubilities were 282, 425 and 194 g/L. The constraints posed by the relatively low bpp solubilities are aligned with efforts to minimize its use due to its waste intensive synthesis. Importantly, replacing DCM with MTBE did not significantly alter the HyFo performance (Figure 1), thus making MTBE a promising solvent option for the preparation and larger-scale implementation of monolithic HyFo SLP catalysts.

Table 1: Catalyst stock solution components

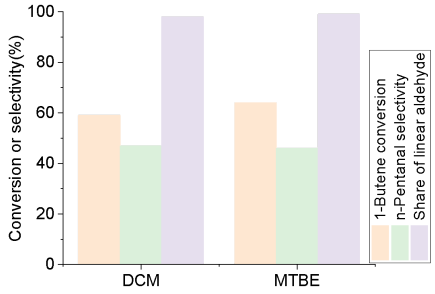

Figure 1: HyFo performance of SLP catalysts produced with DCM or MTBE.

Acknowledgments. *The authors gratefully acknowledge financial support from the European Commission within the Horizon2020-SPIRE project MACBETH under grant agreement N°869896.*

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Supported catalytic active liquid metal solution catalysts on hierarchical SiO_2 supra particles in propane dehydrogenation – effects of support pore size and surface roughness

N. Madubuko[1], D. Lehmann[1], U. Sultan[1], N. Taccardi[1], M. Haumann[1], N. Vogel[1], P. Wasserscheid[1,2*]

[1] *Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen, Germany*
[2] *Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), Erlangen, Germany*
**peter.wasserscheid@fau.de*

Keywords: catalyst, SCALMS, support, dehydrogenation, agglomeration, stability

In several high-temperature applications, heterogeneous catalysts suffer from deactivation, mainly induced by agglomeration and coke deposition (coking). Improving the efficiency and stability of such catalysts is a major challenge. Supported Catalytically Active Liquid Metal Solution (SCALMS) systems offer unique benefits in addressing these challenges.[1] In SCALMS catalysts, small amounts of an active metal (e.g. Pt) are placed in a low melting metal (e.g. Ga) matrix, resulting in liquid alloys at reaction conditions. The unique reactivity and catalytic performance of SCALMS is attributed to the presence of its highly active and dynamic single active sites (Figure 1a).[1-3]

Current synthesis of GaPt-SCALMS by ultrasonication leads to a broad particle size distribution of 0.01 – 1µm. The formed alloy particles are deposited on the external surface of porous supports like SiO_2 and Al_2O_3 with pore sizes in the range of 5 – 15 nm.[3] Under reaction conditions in propane dehydrogenation, the mobility of the GaPt particles on the support's external surface leads to agglomeration and eventual catalyst deactivation.[3,4]

In this contribution, we improve the SCALMS catalyst synthesis technique by systematically controlling the GaPt particle size distribution to obtain alloy particles with mean particle size of 180 nm. These formed alloy particles are impregnated onto µm-sized hierarchal supra particles support with improved surface roughness and pore sizes above 100 nm. The influence of the controlled alloy particle size and the supra particle surface roughness entraps the GaPt alloys and decreases the mobility and agglomeration (Figure 1b). This effect results in stable and selective GaPt-SCALMS catalyst with a 35 % decrease in catalyst deactivation rate.

b

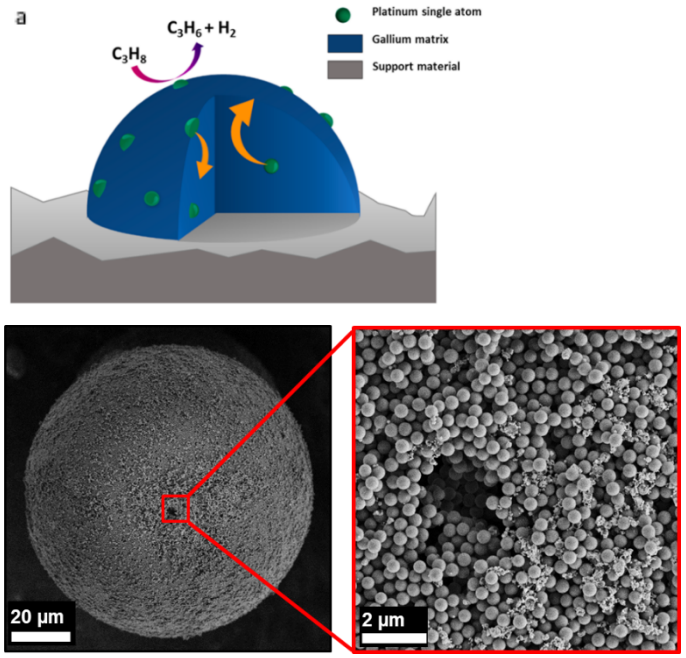

Figure 1a) Schematic illustration of the GAPt-SCALMS principle, b) Scanning electron microscopy (SEM) of GaPt alloy droplets on hierarchal SiO_2 supraparticles with pore size of 300 nm

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MXene mediated layered 2D-3D-2D g-C_3N_4@WO_3@Ti_3C_2 multijunctional heterostructure with enhanced photoelectrochemical and photocatalytic properties

Lekgowa C. Makola [1,2]*, Sharon Moeno [3], Cecil N. M. Ouma [4], Langelihle N. Dlamini [1,2]

[1] *Department of Chemical Sciences, University of Johannesburg, P.O. Box 17011, Doornfontein Campus, 2028, Johannesburg, South Africa.*

[2] *Centre for Nanomaterials Science Research, University of Johannesburg, South Africa.*

[3] *Department of Oral Biological Sciences, Faculty of Health Sciences, University of The Witwatersrand, Johannesburg, South Africa.*

[4] *HySA Infrastructure Centre of Competence, Northwest University, Faculty of Engineering, P. Bag X6001, Potchefstroom 2520, South Africa.*

**Corresponding Author's E-mail address: makolacollen@gmail.com)*

Keywords: ternary photocatalyst, Z-scheme, multijunction heterostructure, WO_3, Ti_3C_2 MXene, g-C_3N_4

Introduction.

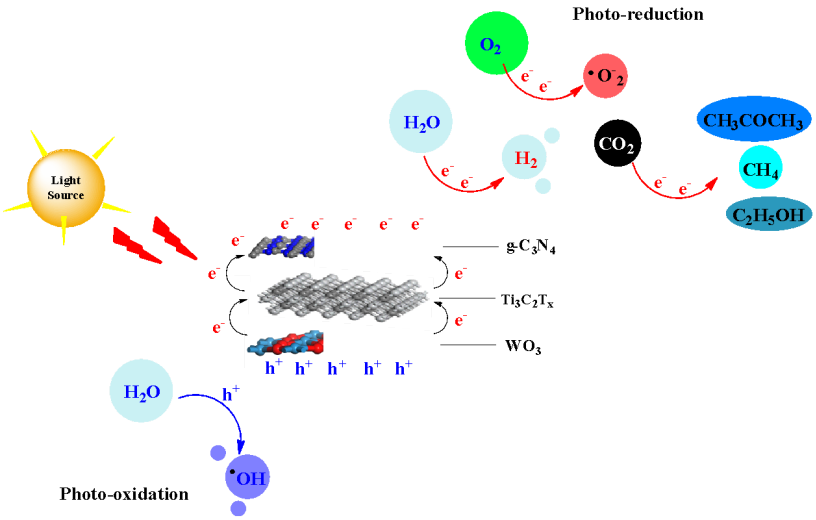
In recent years, advancement in the field of nanotechnology has evolved new strategies to address energy and environmental issues. Amongst the developing technologies, visible-light-driven photocatalysis is regarded as a sustainable approach for energy production and environmental detoxifications, where transition metal oxides (TMOs) and metal-free carbon-based semiconductors such as graphitic carbon nitride (CN) evidenced notable potential in this matter [1-3].

Experimental/methodology.

Herein, g-C_3N_4@WO_3@$Ti_3C_2T_x$ three-component multijunction photocatalyst was fabricated via facile ultrasonic-assisted self-assembly, followed by calcination to facilitate extensive integrations of the materials. A series of different Ti_3C_2 wt% loading in the g-C_3N_4@WO_3@$Ti_3C_2T_x$ were prepared and represented as 1-CWT, 3-CWT, 5-CWT, and 7-CWT corresponding to 1, 3, 5, and 7wt%, respectively. Systematic characterization using spectroscopic and microscopic techniques were employed to validate the successful preparation of the photocatalysts. Enhanced optoelectronic and photoelectrochemical properties were observed for the WO_3@Ti_3C_2@g-C_3N_4 heterostructure with respect to the individual materials.

Results and discussion.

Photoluminescence spectra and Nyquist plots show restrained recombination rates and improved photocarrier conductivities, respectively, and this was credited to the synergistic coupling effect and the presence of highly conductive Ti_3C_2 MXene [4]. The strong interfacial contact surfaces upon the formation of the composite were confirmed using XPS. Multiple charge transfer mechanisms were proposed for the WO_3@Ti_3C_2@g-C_3N_4, which couples Z-scheme and Schottky-junction mediated with Ti_3C_2 MXene. Bode phase plots show improved charge carrier life-times upon the formation of the multijunctional photocatalyst. Moreover, transient photocurrent density of 7-CWT is 40 and seven (7) times higher compared to that of g-C_3N_4 and WO_3, correspondingly. Unlike in the traditional Z-Scheme, the formed ternary heterostructure possesses interfaces through the metallic 2D Ti_3C_2 MXene which provided charge transfer channels for efficient photocarrier transfers with carrier concentrations (N_D) of 17.49×10^{21} cm^{-3} and 4.86% photo-to-chemical conversion efficiency. The as-prepared ternary g-C_3N_4@WO_3@$Ti_3C_2T_x$ exhibited excellent photoelectrochemical properties with reserved redox band potential potencies to facilitate efficient photo-oxidation and -reduction reactions. The fabricated multijunction photocatalyst exhibits potentials to be used in an extensive range of photocatalytic process vis., the production of valuable hydrocarbons from CO_2, production of H_2, and degradation of a plethora of pollutants from wastewater.



Scheme 1. Graphical abstract of the photocatalytic nanomaterial undergoing photocatalysis.

Acknowledgments

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Structural flexibility of the Mn-Ti-based perovskites and activity for the CO oxidation reaction

R. Mane[1], H.-S. Kim[1], K. Han[1],H. Kim[1], Y. Jeon[*,1]

[1] *Department of Environmental and Energy Engineering, Yonsei University, Wonju, Gangwon-do 26493, Republic of Korea*

[*] *Corresponding Author's E-mail address: ykjeon@yonsei.ac.kr*

Keywords: Mn-Ti perovskites, Composition change, CO oxidation

Introduction. Mn-Ti-based perovskite oxides are a category of materials that exhibit structural flexibility, making them appropriate for various applications, including oxidation reactions. These materials can serve as efficient catalysts for a range of oxidation reactions, including environmental remediation, energy conversion, and organic synthesis [1]. The structural flexibility of Mn-Ti-based perovskites allows for tailoring the catalyst's properties by modifying the composition, doping with different elements, or controlling the oxidation state of the metal cations. These modifications can influence the perovskite catalysts' activity, selectivity, and stability, making them versatile for various oxidation reactions. In the present study, stoichiometric and non-stoichiometric Mn-Ti-based catalysts were prepared and a detailed investigation was done for structural alteration and their simultaneous influence on the CO oxidation activity.

Experimental/methodology: The stoichiometric as well as non-stoichiometric $LaSrMnTiO_{3x}$ catalysts were prepared by the traditional solid-state synthesis [2]. The catalytic activity for CO oxidations was performed in a fixed-bed stainless steel tube (9.5-mm inside diameter) reactor. The gaseous products were analyzed by online gas chromatography (Agilent GC 8890) connected with a dual system of a thermal conductivity detector (TCD) and a flame ionization detector (FID) using a Porapak Q column and a Molecular Sieve 5A packed column, respectively.

Results and discussion.

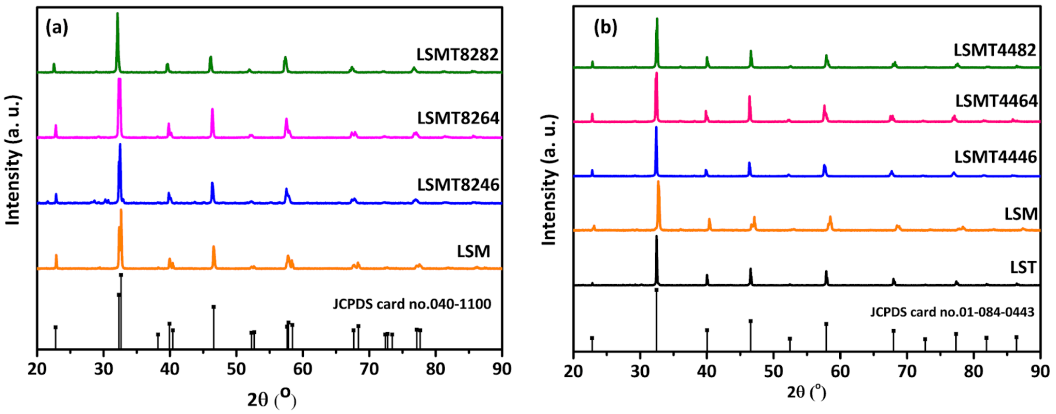

Figure 1. XRD diffraction patterns of $LaSrMnTiO_3$ perovskite, (a) stoichiometric and (b) Non-stoichiometric.

As shown in **Fig. 1** a and b the change in stoichiometry as well as the content of Mn led to a change in the crystal structure of the LSMT perovskites. Stoichiometric LSMT showed the monoclinic crystalline phase of $La_{0.8}Sr_{0.2}MnO_3$ (JCPDS#00-040-1100) having space group P 1 1/c 1 whereas, nonstoichiometric corresponds to the cubic structure of $SrTiO_3$ (JCPDS card no. 01-084-0443) with space group of Pm-3m. With an increase in the Mn content, the crystal structure of stoichiometric perovskite changes from monoclinic to trigonal with simultaneous changes in unit cell parameters. On the contrary in non-stoichiometric catalysts, there were no changes in the crystal structure as well as cell parameters. Further detailed investigations were conducted regarding the Mn oxidation states, the extent of reducibility, different oxygen species, and their consequent impact on CO oxidation activity.

Acknowledgments

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The Impact of Manganese Incorporation on the Activity of Cobalt Spinel Catalysts in Oxygen Evolution Reactions

Saskia Arnold[1], *Anna Rabe*[1,2], *Malte Behrens*[1*]

[1]*Christian-Albrechts-Universität zu Kiel, 24118 Kiel, Germany*
[2]*University of Duisburg-Essen, 45141 Essen, Germany*
[*]*mbehrens@ac.uni-kiel.de*

Keywords: Co/Mn-spinels, OER, CAN test

Introduction. Co-based catalysts have shown promising activity towards chemical or electrochemical oxygen evolution reaction (OER).[1] While pure Mn oxides have relatively low activity in electrochemical OER, higher OER performance of mixed phases of Mn- and Co-based oxides has been reported in the past.[2,3] Therefore, in our work, we investigated the correlation between Mn incorporation into Co-spinel catalysts and the activity in chemical and electrochemical OER.

Experimental/methodology. $Co_{3-x}Mn_xO_4$ spinels with different particle morpholgies were synthesized by calcining the hydroxide (platelets) or hydroxycarbonate precursors (spheres) at 400 °C or 500 °C in air for 3 h. The precursors were prepared via co-precipitation in an automated synthesis station using NaOH or Na_2CO_3 as precipitation agent at a constant pH of 8.5 or 9. For the chemical OER, CAN test was performed: A 2.5 M $(NH_4)_2Ce(NO_3)_6$ solution was added to a dispersion of catalyst in water and the oxygen evolution was monitored for 2 h. Electrochemical OER was carried out in a three-electrode cell with 1 M KOH as electrolyte.

Results and discussion. $Co_{3-x}Mn_xO_4$ catalysts with anisotropic and isotropic particle morphologies were synthesized via co-precipitation and subsequent thermal decomposition. The phase purity of the catalysts was proven by powder X-ray diffraction (XRD) (Figure 1a). In addition, a shift of the reflections towards smaller 2θ values could be observed, indicating Mn incorporation. The Mn content and the particle morphology were confirmed experimentally. For electrochemical OER, a trend independent from spinel morphology was observed: the overpotentials were decreasing for both series with ~2.5% Mn and again increasing for ~7.5% Mn showing higher activity for the samples with lower Mn content (Figure 1b). In contrast, morphology seemed to have a bigger influence on the CAN test: As the Mn content increased, the initial rates for the isotropic samples decreased, while those for the anisotropic samples initially decreased and then increased for the 7.1%-sample. The results may be explained with an opposing effect of the catalyst's mesostructure on its specific surface area and its electric conductivity.[4]

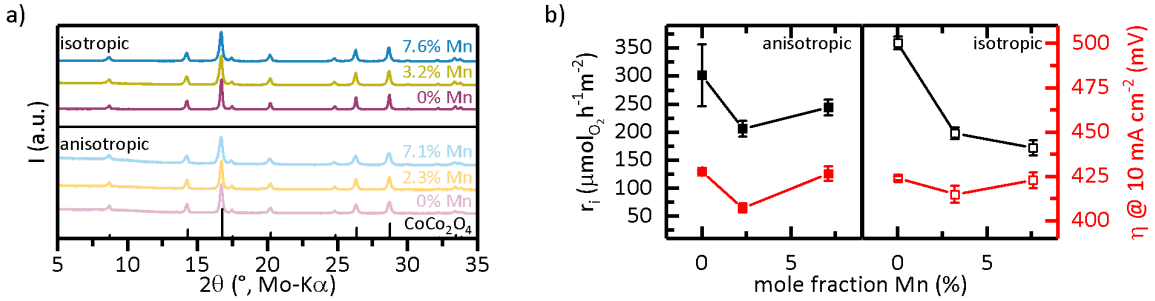

Figure 1: a) XRD pattern of the synthesized Co/Mn-spinels in comparison the pattern of $CoCo_2O_4$ (black; ICSD No. 150805)[5]. b) Comparison of the initial rate r_i (black) and the overpotential η (red) at 10 mA cm^{-2} determined for the Mn-substituted Co-spinels normalized to the BET surface area.

Acknowledgments

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Stability of gold-functionalized catalysts in glucose oxidation

A. Ciemięga[1], K. Maresz[1*], M. Romaszewski[2], P. Głomb[2], P. Krupska-Wolas[3], K. Prusik[4]

[1] *Institute of Chemical Engineering Polish Academy of Sciences, Gliwice, Poland*
[2] *Institute of Theoretical and Applied Informatics Polish Academy of Sciences, Gliwice, Poland*
[3] *Laboratory of Analysis and Nondestructive Investigation of Heritage Objects, National Museum, Kraków, Poland*
[4] *Institute of Materials Engineering, University of Silesia, Katowice, Poland*
*(*maresz@iich.gliwice.pl)*

Keywords: gold nanoparticles, glucose oxidation, porous silicas

Introduction. Pore structure and texture parameters of support are crucial to develop an appropriate size and dispersion of gold nanoparticles (AuNPs), which translates directly to their catalytic activity and stability. It was reported that AuNPs smaller than 10 nm are highly active in oxidation processes [1]. However, their application is often limited by deactivation resulting from agglomeration, poisoning and changes of the oxidation state of the gold.

In this work, modified silica materials of various pore characteristics were used as AuNPs carriers to study the relationship of materials structure - AuNPs size/dispersion - catalytic activity/stability.

Experimental/methodology. Micro- and mesoporous silicas with pores in the range of 1.5 – 30 nm were obtained and functionalised with alumina and propylamino groups. AuNPs in the amount of 0.5, 1 and 2% wt. were deposited via the direct reduction method [2]. Materials were characterized using low-temperature nitrogen adsorption, TEM, UV-Vis spectroscopy and hyperspectral imaging. The catalytic properties were tested in glucose oxidation with oxygen in a batch reactor, and catalysts were recycled five times.

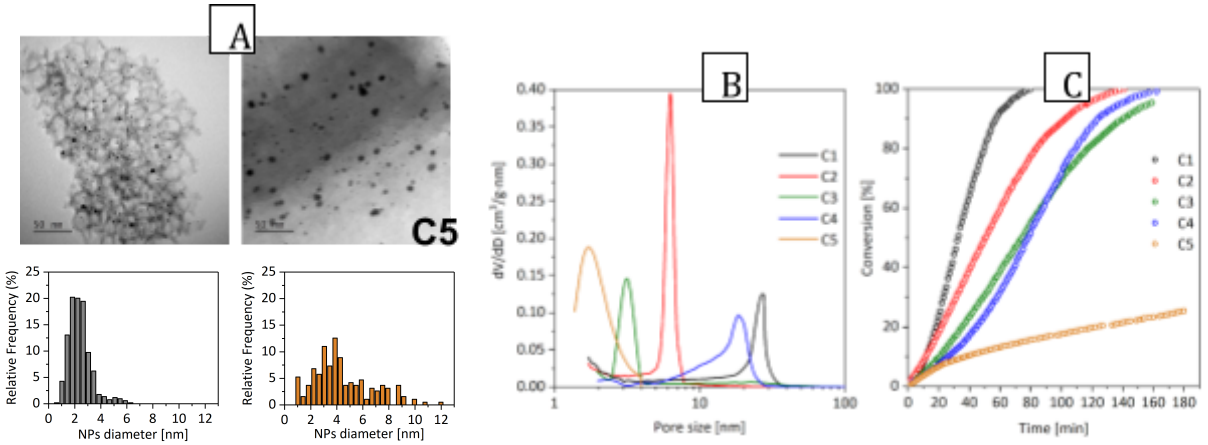

Figure 1. TEM images and AuNPs particle size distribution in catalyst C1 and C5, B) pore size distributions in catalysts, C) conversion of glucose in 1st run of oxidation process

Results and discussion. The size and dispersion of AuNPs strongly depended on the porous structure of the silica supports (Fig. 1A). The performance of the glucose oxidation coraborated well with the size distribution/dispersion of AuNPs and diffusion of substrates, which was limited by the size od pores (Fig. 1 B, C). It was shown that the pore size distribution in a support has siqnificant impact on the stability of deposited AuNPs, and thus on the performance of oxidation process. The most stable catalyst appeared to be that of the hexagonally ordered pores with diameter of about 6 nm. Moreover, a hyperspectral camera was proved to be an effective tool to follow the changes in the size of supported gold nanoparticles.

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Selective hydrogenation and hydrodeoxygenation using bimetallic Fe_xPt_{100-x} nanoparticles immobilized on supported ionic liquid phases

Nataliia Marchenko[1*], Simon Tricard[1], Alexis Bordet[2], Walter Leitner[2]

[1] *Laboratoire de Physique et Chimie des Nano-Objets INSA, 135 Avenue de Rangueil, 31077 Toulouse, France;*

[2] *Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34-36, 45470 Mülheim an der Ruhr, Germany;*

**marchenk@insa-toulouse.fr*

Introduction. For decades selectivity remains a main challenge in heterogeneous catalysis. Considering this issue NPs immobilized on supported ionic liquid phases (SILP) present an elegant solution since by easy modification of a structure of an ionic liquid, nature of metal NP or nature of support it is possible to activate specific functional groups leaving others untouched. Moreover, the use of bimetallic catalysts has the potential to afford high activity with the possibility to control selectivity in hydrogenation by adjusting ratios of metals in the catalyst[1]. In the present study, we aim at preparing bimetallic iron-platinum nanoparticles (Fe_xPt_{100-x} NPs) combining the excellent hydrogen activation capability of platinum with the oxophilicity of iron to achieve the effective and selective hydrogenation and hydrodeoxygenation of C=O bonds.

Experimental/methodology. Fe_xPt_{100-x}@SILP were synthesized by decomposition of organometallic precursors of Fe ([bis(trimethylsilyl)amide]diiron (II)) and Pt (tris(dibenzylideneacetone)diplatinum (0)) in H_2 atmosphere in presence of the SILP (Figure 1a). This organometallic approach allowed precise control of the composition of bimetallic NPs (Fe_{100}, $Fe_{80}Pt_{20}$, $Fe_{60}Pt_{40}$, $Fe_{50}Pt_{50}$, $Fe_{40}Pt_{60}$, Pt_{100}). Morphology, NPs size (around 2 nm) and dispersion were studied by TEM and HR-TEM. Metal loading and ratio were confirmed using SEM-EDX. The oxidation states of metals were analyzed with XPS. FT-IR of Fe_xPt_{100-x}@SILP after CO adsorption was conducted as well. The analysis revealed electron density transfer from Fe to Pt sites that can be a reason for high selectivity in C=O hydrogenation.

Results and discussion. The reactivity of Fe_xPt_{100-x}@SILP catalysts was probed using the hydrogenation of acetophenone as a model reaction. The activity and selectivity of Fe_xPt_{100-x}@SILP catalysts were highly dependent on the Fe:Pt ratio. In particular, Pt@SILP led to the full hydrogenation of acetophenone to give the saturated alcohol in quantitative yield, while the incorporation of Fe in $Fe_{40}Pt_{60}$@SILP resulted in the hydrodeoxygenation of the ketone with conservation of the aromatic ring. The scope was extended to para-substituted acetophenones where excellent selectivities towards HDO products were reached (Figure 1b). Moreover, $Fe_{40}Pt_{60}$@SILP catalyst was used in the hydrogenation of a model unsaturated aldehyde – cinnamaldehyde. High selectivity toward unsaturated alcohol was achieved and remained after an extended reaction time (Figure 1c). These results illustrate that precise control of bimetallic NPs composition and structure can lead to high activities and tailor-made selectivities towards challenging products.

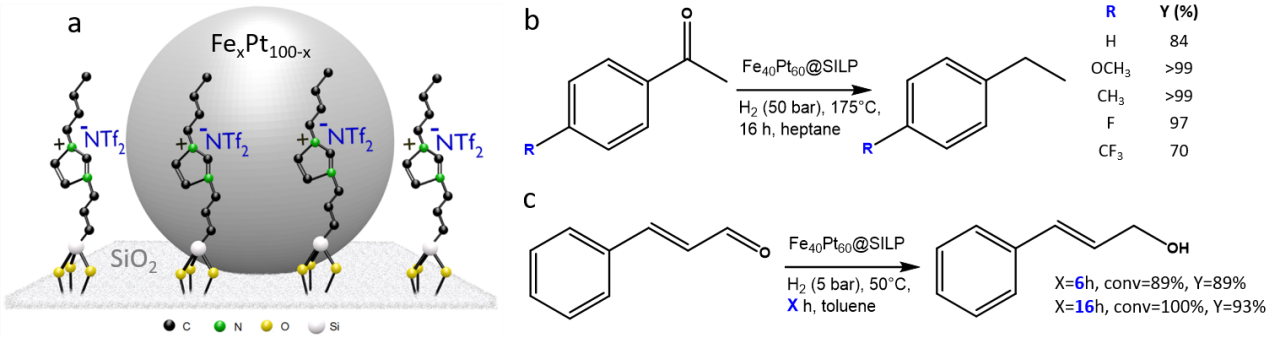

Figure 1 a) Illustration of Fe_xPt_{100-x}@SILP system; b) hydrogenation of acetophenone; c) hydrogenation of cinnamaldehyde.

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Improved synthesis of nano Chevrel Phases for alkaline HER

Alexander M. L. Frisina[1], Anthony F. Masters[1], Thomas Maschmeyer*[1]
Laboratory of Advanced Catalysis for Sustainability, University of Sydney, Australia

Keywords: Hydrogen, Electrocatalysis, Molybdenum Sulfide, Chevrel Phase, Hydrothermal, Nanoparticles

Introduction. The production of hydrogen (H_2) from water (H_2O) using electrolysers is projected to become more common at commercial scale as the world seeks to decarbonise. It is vitally important to research new catalysts to supply the required electrolysers, and improve electrolyser performance.[1] Chevrel Phases (CPs) of type MMo_6S_8 (M = guest transition metal ion) are promising alternative catalysts to produce H_2 through electrocatalytic reactions.[2] However, their large particle size prevents full realisation of their electrocatalytic activity.[2] The discovery of reliable methods to create nanoparticulate CPs would allow chemists to fully explore CPs as next generation electrocatalysts.

Experimental/methodology. Starting materials: **Nano Cu CP***:* $CuNH_4MoS_4$, $N_2H_4{\cdot}H_2O$ and H_2O *OR* **Nano CP Variants***:* Layered transition metal material (*e.g.* $Ni(OH)_2$), $(NH_4)_2MoS_4$, $N_2H_4{\cdot}H_2O$ and H_2O. The starting materials were heated to 200 °C in a sealed vessel under N_2 (1.72 bar) for 20 hours, reaching a max stable pressure of 18 bar. The resulting powder was isolated then treated in a furnace for 60 hours under 5% H_2/Ar, yielding nano Chevrel Phase material. Cu CP was deintercalated using HCl (1 M) and O_2 to give nano Mo_6S_8. CP electrocatalysts were prepared *in situ* by intercalation of nano Mo_6S_8 to give MMo_6S_8 (M=Ni, Cu, Zn) at a potential determined by cyclic voltammetry (CV). Linear sweep voltammograms (LSVs) were performed in 0.1 M NaOH according to procedures used in our laboratory.[2]

Results and discussion. Our findings were two fold. Firstly, we reported the hydrothermal preparation of nano CP precursors allowing the inclusion of a variety of transition metals in CP guest sites (Figs. 1a, 1b). This may prove to be the first method of nano CP synthesis that can be generalised to several guest metals. Secondly, our preliminary electrochemical investigations have revealed that nano Ni CPs may break a previously held belief that CPs containing guest ions are worse catalysts for the hydrogen evolution reaction than bare Mo_6S_8 (Fig. 1c).[2]

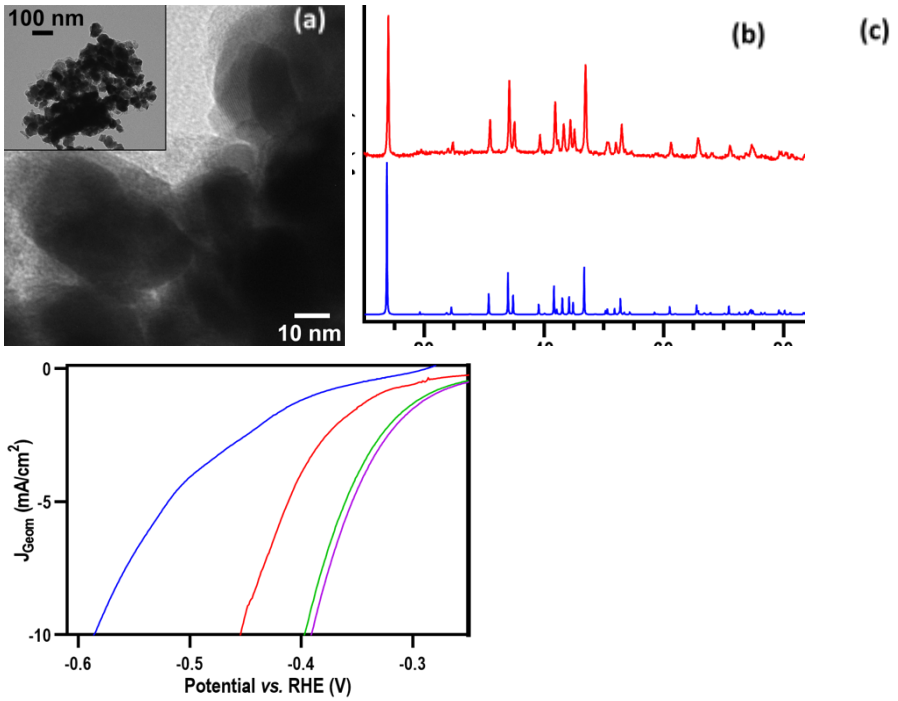

Figure 1: (a) TEM micrograph of nano Cu CP particles. (b) Powder XRD pattern for nano (red) and literature (blue) Mo_6S_8,[3] λ = 1.5406 Å. (c) Alkaline LSV (pH = 13) screening tests for nano NiCP (purple), ZnCP (blue), CuCP (red) and bare Mo_6S_8 (green). Scan rate 50 mV/s, performed under blanket N_2, working electrode A_{Geom} = 0.071 cm^2. Reference electrode: Ag/AgCl 3 M KCl, counter electrode: graphite. Potentials corrected by $E_{RHE} = E_{Ag/AgCl} + 0.210\ V + pH*0.059\ V$.

Acknowledgments

We acknowledge the Gadigal of the Eora nation, the traditional custodians of the land that now houses the University of Sydney School of Chemistry. We also acknowledge the contributions of Dr Samuel Duyker for assistance in X-ray Diffraction measurements and Dr Hongwei Liu for assistance in TEM.

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Immobilization of Ni complexes in hydrophobic materials for ethylene oligomerization

Mathieu Lions[1], Dr. Jérôme Canivet[1], Dr. Alain Tuel[1] et Dr. David Farrusseng*[1]

[1]*Université Lyon 1, CNRS, IRCELYON – UMR 5256, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France*
**david.farrusseng@ircelyon.univ-lyon1.fr*

Keywords: Hydrophoc zeolites, core-shell structures, complex immobilization, ethylene oligomerization.

Introduction. The dimerization and oligomerization of light olefins is an important route to produce linear and branched higher olefins. Transition metal based molecular complexes are performing catalysts towards butenes or linear alpha olefins (LAOs) C_4, C_6 and C_8 which are the main products of interest. Nevertheless, in such industrial processes, the catalyst is lost in the products and therefore cannot be reused nor recycled. It was found that Ni-exchanged zeolites can dimerize ethylene to light hydrocarbons [1, 2]. Indeed, the encapsulation of an active and selective molecular catalyst in a porous scaffold usually appears as an elegant heterogenization process. However, loss of catalyst activity and/or selectivity upon encapsulation is often reported as main limitation of this heterogenization approach. The objective of this work is to demonstrate that molecular catalyst encapsulation in hierarchical porous zeolites can afford efficient catalysts for ethylene oligomerization.

Experimental/methodology. We have chosen Ni-2,2'bipyridine (Nibipy) molecular complex for well-known activity and as its dimension can be compatible with cavity size of zeolites. As hosts, we have synthesized and selected commercial medium to large pore zeolites (MFI, BEA and FAU). For Faujasites, commercial CBV samples (from zeolyst) were used post-treated as received. Additionally, a hollow faujasite was synthesized according to a previous work [3]. The encapsulation process is a two steps synthesis. First, exchange of compensating cations by Ni cations followed by complexation with 2,2'bipyridine. The characterization of Ni-2,2'bipyridine complexes in zeolites was achieved by combining TGA, Infrared-, UV-visible spectroscopies and N_2 physisorption measurements. Finally, the oligomerization of ethylene was carried out in batch reactors at 308K and 30 bars for 1h in n-heptane (n_{Ni} = 10 µmol) in the presence of Et_2AlCl as cocatalyst (100 eq.)

Results and discussion. The confirmation of Ni-Ligand formation in the pore cavities and also importantly the ligand to Ni ratio are important. Indeed, we have found that for molecular catalysts, only the 1:1 ratio is very active. Consequently, it was necessary to control this ratio during the immobilization of the complex in the different supports in order to optimize the catalytic activity. In addition to that, we propose that the activity increases after complexation and with the creation of mesoporosity and macroporosity. Moreover, the selectivity towards branched olefins seems to enhance with the porosity. This may be explained by increasing the number of silanol defects during the creation of larger porosity by dealumination. Finally, these trends were observed when comparing plain and hollow zeolites of MFI and BEA topologies.

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Dealumination of USY for stabilization of subnanometric reducible metal oxide nanoparticles

Ang Li[1], Yuyan Zhang[1], Muhammad Numan[2], Jiři Čejka[1], Changbum Jo[2], and Michal Mazur[1]

[1] *Department of Physical and Macromolecular Chemistry, Charles University, Hlavova 8, 12800 Prague, Czechia*
[2] *Department of Chemistry and Chemical Engineering, Inha University, Incheon 22212, Republic of Korea*

Keywords: Zeolites; Pd nanoparticles; dry methane reforming; metal-silanol interactions; sintering resistance.

Introduction. Metal nanoparticles encapsulated into zeolite matrix are efficient heterogeneous catalysts. Advantages of zeolites as supports are their high surface areas, rigid porous structures, physical and chemical stability, and tunable acid sites. [1]. Most of current synthesis strategies highly rely on the usage of protective organic ligands, which is expensive and not eco-friendly approach. [2] Facile and sustainable scale-up of metal@zeolite materials synthesis is highly desired. Recently, Ryoo et al. [3] and Yu et al. [4] reported the confinement of nanosized metal clusters in nanosponge MFI zeolites by post-synthesis method (wet impregnation). Resulting materials possess uniform small metal clusters evenly distributed and showing good thermal stability.

Herein, we utilize commercial zeolite as the parent material for and creation of silanols by dealumination. Subsequently, simple impregnation and calcination, the final materials possess a good dispersion of subnanometric metal particles on the materials and uniform size distribution. In contrast to the previous report, our strategy avoids the employment of expensive non-recycled organic SDA. This breaks the limitation for larger scale usage in a possible industrial scenario.

Experimental/methodology. Zeolite support (denoted as deAl-USY) had silanols generated throughout acid dealumination of commercial zeolite USY (CBV-720, Si/Al=15, zeolyst). The Pd@deAl-USY and Pd@USY were synthesized via a facile impregnation followed by calcination.

Results and discussion. We investigated the thermal stability of Pd nanoparticles in different support by performing *in-situ* step-wise heating (from the room temperature up to 700 °C) in scanning transmission electron microscope (STEM). Properties of prepared materials were investigated by PXRD, Ar sorption, SEM, and XANES. Obtained materials were tested in the dry reforming of methane at 600 °C. Catalytic results reveal that Pd@deAl-USY shows a longer lifetime and higher methane conversion compared with Pd@USY. This could be attributed to the improved thermal stability of Pd in silanol-rich Pd@deAl-USY.

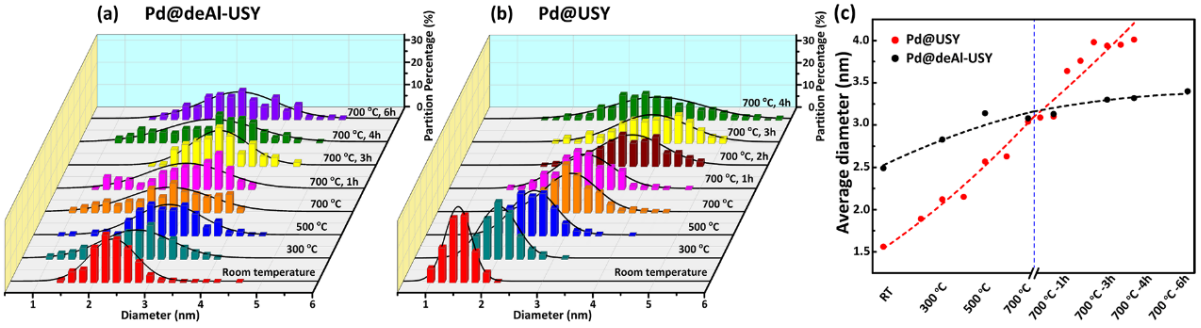

Figure 1. *Pd particles size distributions evolution of Pd@deAl-USY (a) and Pd@USY (b) during heating; (c) Average sizes of Pd from in-situ heating STEM imaging.*

Acknowledgments

Authors acknowledge support of the Czech Science Foundation for the project ExPro (19-27551X). M. Numan and C. Jo acknowledge the support from National Research Foundation of Korea.

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Development and up-scaling of iron-based catalysts for sustainable Fischer-Tropsch synthesis of higher alcohols

M. Medicus[1*], J. Mettke[1], E. Reichelt[1], M. Jahn[1]

[1]*Fraunhofer Institute for Ceramic Technology and Systems IKTS, Dresden, Germany*
[*]*maximilian.medicus@ikts.fraunhofer.de*

Keywords: Fischer-Tropsch synthesis, catalyst scale-up, structured catalyst, process integration, promotion, catalyst support, higher alcohols

Introduction. Due to depletion of fossil feedstocks and regulations concerning CO_2 emission reduction goals, mobility and chemical sector demand for new production pathways towards fuels and fine chemicals. Focusing on carbon feedstocks like waste, biogas or CO_2 chemicals can be produced in two-step approaches combining syngas production via gasification, biogas reforming or co-electrolysis of H_2O and CO_2 and subsequent Fischer-Tropsch synthesis [1]. Prospects for short- to mid-term economic feasibility are better for high-margin chemicals like higher alcohols (HA), being linear 1-alcohols with more than 4 C-atoms per molecule. Promising and tunable selectivity for HA was confirmed for cheap bulk iron powder catalysts but structuring and scaling has been neglected so far [2]. Herein we present the development of scaled and optimized iron catalysts operated with sustainably sourced syngas under statistically optimized reaction conditions in easy-to-scale fixed-bed reactors to allow for the assessment of the process potential.

Experimental/methodology. Bulk iron catalysts were produced by co-precipitation and promoted by incipient-wetness impregnation (IWI). Supported powder catalysts were fabricated and promoted by IWI of different support materials. Recipes for thermoplastic extrusion of pellets were developed and optimized. The optimized catalyst was investigated under varying operation conditions adding 10 % CO_2 mimicking the typical composition of sustainable syngas. A predictive model for performance depending on conditions and TOS was developed. Experiments on tail gas recycling in a scaled reactor setup were conducted to increase overall conversion. Fresh and spent catalysts were extensively characterized.

Results and discussion. For bulk iron catalysts besides the known promoters K, Cu, Mo, Li was found to significantly improve catalyst activation, CO conversion and HA selectivity. Its effect could be exploited on powder and structured Al_2O_3-supported catalysts, while beneficial effects of other promoters did leak expectations. Besides Al_2O_3, ZrO_2 and SiC were found to be promising structural promoters and structural performance descriptors were identified. Presence of 10 % CO_2 in the syngas feed caused a significant decrease in conversion and HA selectivity. Nevertheless, precise tuning of reaction conditions and data analyses by statistical methods allowed for a model-based prediction of promising condition sets, that were experimentally confirmed giving CO conversion of 25-30 % at HA selectivity of 10 %, outperforming powdered catalysts. Even though slight deactivation occurred, the optimized catalyst could be fully reactivated after 2000 h TOS. For the first time tail gas recycling experiments were conducted on an optimized shaped iron catalyst allowing for a HA yield of 8 % which is 3.5 times the highest value reported so far for iron-based HA synthesis [2-4]. Options for further yield increase are discussed in the outlook. However, also the by-products can be fed to existing petrochemical pathways for additional value creation. The results also allowed to gain basic data for the assessment of the complete production process of HA.

Acknowledgments
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An improved preparation method for a CuO/CeO_2-coated monolith for the CO-PrOx reaction

Jan Meißner[1*], Lara Ahrens[2], Joachim Pasel[1], Alexander Schwedt[2], Sebastian Wohlrab[3], Joachim Mayer[2] and Ralf Peters[1]

[1] *Forschungszentrum Jülich, Institute of Electrochemical Process Engineering (IEK-14), Jülich, Germany*

[2] *RWTH Aachen University, Central Facility for Electron Microscopy, Aachen, Germany*

[3] *Leibniz Institute for Catalysis, Rostock,Germany*

[*] *j.meissner@fz-juelich.de*

Introduction. To run a PEM Fuel Cell, a H_2-rich fuel gas is produced from liquid fuels like diesel or kerosene using the fuel processing technology. The initial step of fuel processing is reforming, followed by the water-gas shift reaction [1], which reduces the CO concentration in the product gas from reforming to below 1 vol.%. To operate a PEMFC, however, the concentration of CO needs to be lowered below 100 ppm [1, 2]. Typically, this is accomplished using the PrOx (preferential oxidation) reaction. This paper reports on an improved method for the preparation of a CuO/CeO_2 based monolithic catalyst for the Prox-reaction.

Experimental/methodology. Using Avgouropoulos' et al. [3] work in particular, ceramic monoliths (cordierite, 400 cpsi honeycomb structure) were coated directly with a mixed oxide of CuO/CeO_2. No washcoat was applied. Instead, the monoliths were dipped twice in a viscous precursor solution and calcined at 450°C. Thus, the catalyst was directly formed on the cordierite surface. The catalyst was characterized by means of XRD, SEM/EDX, and EPR.

Results and discussion.

Experiments were conducted with a dry (FG1: 39 vol.% H_2, 20 vol.% CO_2, 1 vol.% CO, balance: N_2) and a moist fuel gas (FG2: 35 vol.% H_2, 16 vol.% CO_2, 1 vol.% CO, 20 vol.% H_2O, balance: N_2). Fig. 1a and 1b depict the CO conversions using FG1 and FG2, respectively, as a function of the temperature at varying space velocities (GHSV). With FG1 X(CO) was > 99 % up to GHSV=5,000 h^{-1}. At 10,000 h^{-1} a marginally lower maximum of 97% was observed. Slightly different CO conversions were observed in the presence of steam (cf. Fig. 1b). The temperature interval of maximum CO conversions became smaller while the temperature level increased. It is assumed by Zou et al. [4] that a competing adsorption of H_2O on the catalytic sites of CuO/CeO_2 catalysts and the formation of H_2O/CO surface complexes causes the inhibition of the CO oxidation.

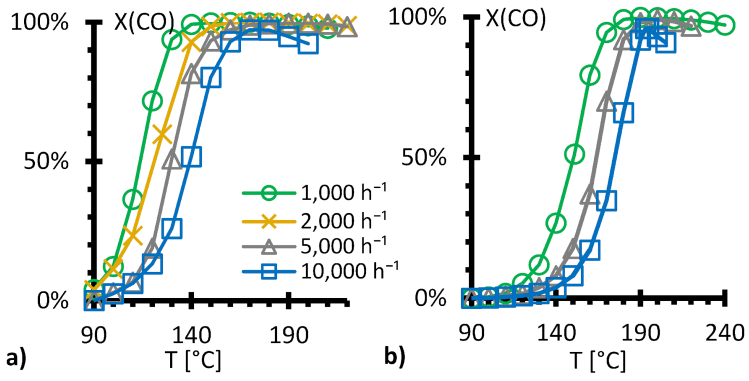

Figure 1. CO conversion as a function of the temperature with varying values for the GHSV at λ = 2.5, a) dry fuel gas (FG1), b) moist fuel gas (FG2).

In addition, a long term test for 311 h was carried out with FG2. The temperature at which the maximum conversion could be achieved marginally rose from 193 °C to 203 °C at the end of the run. In parallel, the maximum CO conversion decreased by 1.4 percentage points from 96.8% to 95.4%. It can be concluded that the application of the new preparation method for the monolithic CuO/CeO_2 was successful.

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Towards a Machine Learning Model for Zeolite Synthesis

D.P. Costa, L. Frazão, M.F. Ribeiro, P.S.F. Mendes

Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, Lisbon 1049-001, Portugal

Keywords: Zeolite, Synthesis, Machine-Learning, Model

Introduction.

Zeolites are crystalline aluminosilicate featuring a well-defined 3D structure with micropores and acid sites, both key to its catalytic success, but not straightforward to tune since the physical processes that occur during the zeolite synthesis are very complex and difficult to describe.[1] Nowadays zeolite tunning to a given set of properties is made via time-consuming trial and error. Model-based optimization can potentially provide clear synthesis guidelines for a target set of properties. However, fundamental (white) modelling of the zeolite synthesis process is hampered by its complex nature. Hence, the objective of this work is to develop a sound black-box model correlating the synthesis conditions with the zeolite properties.

Experimental databases.

Two different datasets needed to be created. Since machine learning algorithms need a large amount of data and some convergence problems could happen, a dataset of artifical data needed to be created to test how the choosen algorithms describe the desired patterns. This dataset nedded to mimic the patterns found after a litterature analysis between preparation conditions and zeolite properties by using previously known empirical functions for key parameters. The choosen functions needed to represent the expected non-linearity of the complex physical processes involved. Then a dataset containing the zeolite textural, acid and strucutural properties and their respective synthesis conditions, needed to be obtained by using data from scientific papers.

Machine learning.

Some machine learning algorithms have been recently benchmarked already for catalysis by some of us [2]. The starting point will thus be the pool of successful tecnhiques, i.e. artificial neural networks and random forest regression. These will be applied to the artificial dataset to determines which algorithms describe better the high non-linear patterns specific of the relationship between zeolite synthesis-properties. After that, the real dataset should be analyzed to understand the key variables that should be modelled and the degree of the model complexity required. The qualitative assessement of key variables must be done by clustering and dimensionality reduction, while the main trends between sythesis conditions and zeolite properties must be identified by quantitative trend analysis. Then, the machine learning algorithms that showed the best performance with the artificial dataset needed to be used to create the model using the real dataset.

Conclusion.

In conclusion, this develops a sound approach to create a model correlating the zeolite proparation condtions and their properties. This way, a step further can be taken in order to controll the zeolite synthesis, which to this day is not fully understood. Having such a model will facilitate the optimization of novel zeolite catalysts in old and new chemical processes. In the future, it is expected that this model is tested and improved with experimental data.

Acknowledgments

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MOF(Al)-derived catalysts with enhanced activity in CO_2 methanation

M. Mihet*, A.M. Kasza, O. Grad, A. Turza, M. Dan, M.D. Lazar

National Institute for Research & Development of Isotopic and Molecular Technologies – INCDTIM, 67–103 Donat Str., 400293 Cluj–Napoca, Romania
**Corresponding author: maria.mihet@itim-cj.ro*

Keywords: MIL-53(Al)(as), MIL-53(Al)-derived Ni catalysts, CO_2 methanation.

Introduction. Despite the unique properties of metal-organic frameworks (MOFs) such as very high surface area, large porosity in the micro- and meso range with a well-defined pore size distribution, as well as compositional versatility which make them attractive for a multitude of applications, their use on a large scale is limited due to their low stability when exposed to moisture or higher temperatures. However, when used as templates/precursors, MOFs can be transformed into more stable porous materials which inherit to a large extent the properties of the initial MOF [1]. Thus, MOF-derived materials are envisaged as promising candidates in different areas, especially in catalysis, owing to the abundant and well-dispersed active sites that can be obtained in this way. Recently, we have shown that Ni deposited on alumina derived from either the as-synthesized (*as*) or the activated (*lt*) form of MIL-53(Al), a microporous flexible Al-based MOF, leads to catalysts with enhanced performance in the CO_2 methanation process as a result of improved structural and functional properties [2]. The aim of this work is to report on a different approach to obtain MIL-53(Al)-derived Ni catalysts, that is deposition of the metal through the metal salt of choice directly on the as-synthesized MOF, followed by the thermal treatment which allows both the decomposition of the MOF to alumina and of the Ni salt to NiO. The advantage of using directly the (*as*) form relies on the fact that the long and tedious activation procedure can be thus avoided.

Experimental/methodology. MIL-53(Al)-derived Ni catalysts (10wt.% loading) were obtained by metal deposition either by the incipient wetness impregnation method (IWI), or the melting infiltration procedure (MI) on the as-synthesized (*as*) and activated (*lt*) forms of MIL-53(Al) which was synthesized by a less energy and time-consuming approach (190°C, 12 h). The derivation sequence performed at 600°C, for 5 h (0.5°C/min) allowed the concomitant decomposition of MIL-53(Al) to Al_2O_3 and of the starting Ni salt, to NiO. All samples were further reduced in H_2 flow, at 750°C. Characterization was performed by XRD, N_2 sorption isotherms (BET), TPR, TEM/EDX, H_2, and CO_2-TPD. The catalytic performance in the methanation of CO_2 was investigated under plug-flow conditions at atmospheric pressure, in the 200 – 500°C temperature range, $CO_2/H_2/Ar$ = 1/4/1, 36 L g^{-1} h^{-1}, while effluent gases were analyzed by GC equipped with a TCD.

Results and discussion. Characterization results revealed that besides the MIL-53(Al) form used as starting material (either *as* or *lt* form), both the employed deposition technique, and the time have an important impact on the structural, morphological, and functional characteristics of the MIL-53(Al)-derived Ni samples. Thus, small, and very well-dispersed Ni nanoparticles are obtained using the IWI technique on MIL-53(Al)(lt) or the MI method on MIL-53(Al)(as) (< 7 nm). On the other hand, the longer the time used in the case of the MI method, the smaller the deposited Ni nanoparticles, and the less reducible the initial NiO. All samples exhibit lower surface areas than the starting microporous MIL-53(Al), but larger pore volumes, while pore size distribution proves their mesoporous structure. Temperature-programmed desorption of either H_2 or CO_2 reveals an enhanced adsorption capacity of the MIL-53(Al)-derived Ni catalysts as compared to the reference Ni/Al_2O_3 prepared by impregnation of commercial γ-alumina, with consequent improved catalytic performance in the CO_2 methanation process.

Acknowledgments

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Multicomponent monolithic catalysts prepared in 3D printing assistance for oxidative coupling of methane

P. Michorczyk[1*], E. Bogdan[1], M. Nowakowska[1], M. Myradova[1], A. Rokicińska[2], P. Kuśtrowski[2]

[1]*Department of Organic Chemistry and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland*
[2]*Department of Chemical Technology, Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland*
[*]*piotr.michorczyk@pk.edu.pl*

Keywords: Olefins, 3D printing, casting, oxidative coupling of methane

Introduction. 3D printing give possibility of the creation of almost any physical object from a digital 3D CAD (Computer Aided Design) model. In a typical scenario, the digital 3D model is converted to STL (STereoLithography) format and then sliced into a series of two-dimensional layers using specialized software. The 3D printer then builds the corresponding physical object by deposition of a material (e.g. polymers, metals, ceramics and others), using a layer-by-layer approach. The fast development of 3D printing technology observed in the last decade has led to a wide array of promising applications in various fields. In the catalysis 3D printing technologies were used to fabrication of electrochemical electrodes which are the platform of various catalytic device, supports as well as heterogeneous catalysts [1,2].
In this communication we demonstrate that a high resolution 3D printer using DLP (Digital Light Processing) technology can be a useful tool for the preparation of multicomponent monolithic catalysts.

Experimental/methodology. Casting pathway was applied for multicomponent catalysts preparation. In this approach a polymeric matrix, projected as a 3D digital model and then printed with high resolution in DLP technology, can be used as a hard template in order to control the shape and size of channels in monoliths. Based on these templates, a series of Mn, Na, W, Al and Si containing catalysts were prepared. The catalytic performances of the prepared monoliths were investigated in the oxidative coupling of methane (OCM). The conditions and procedures are described previously [3].

Results and discussion. Among many effective OCM catalysts, multicomponent Mn-Na_2WO_4/SiO_2 system is considered to be one of the most promising for practical application due to its high activity, selectivity to C_{2+} and reasonable stability. Typically, in flow type reactors (T = 750–850 °C, CH_4:O_2 = 2.0–4.0, GHSV = 2000-36000 h^{-1}), the selectivity to C_{2+} is in the range 60–80% when CH_4 conversion varies between 20–30 %. [4]. The rational design of monoliths allows to obtain a similar or higher yield of C_{2+} (ethane, ethene, propane and propene) at the range of GHSV compared to powder catalysts. Additional benefits of the developed monoliths are higher selectivity towards C_{2+} (5-7 %) and much lower drop of pressure vs. GHSV. Moreover, we have found that in the catalyst formulation studied the presence of W is not crucial for catalytic performance in OCM. The monoliths with Mn loading of 2-10 wt. % exhibit as high activity as monoliths containing additionally Na_2WO_4. It seems that the presence of both Mn and Na in the monolith composition is necessary for activity as well as high selectivity towards C_{2+} hydrocarbons. Moreover, we have found that controlling of channels size and density in the monoliths allow to control of methane and oxygen conversion and, to a lesser extent, the selectivity to C_{2+}. The catalytic behaviour varies with feed gas composition and GHSV. Under the OCM conditions tested in this work, it is preferable to select the monoliths with moderate channel diameters (0.6-0.8 mm) and as high as possible channels density.

Acknowledgments
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Enhanced CO Oxidation Activity on Perovskite Derived Needle-like $MnO_x/LaMnO_3$ Catalysts

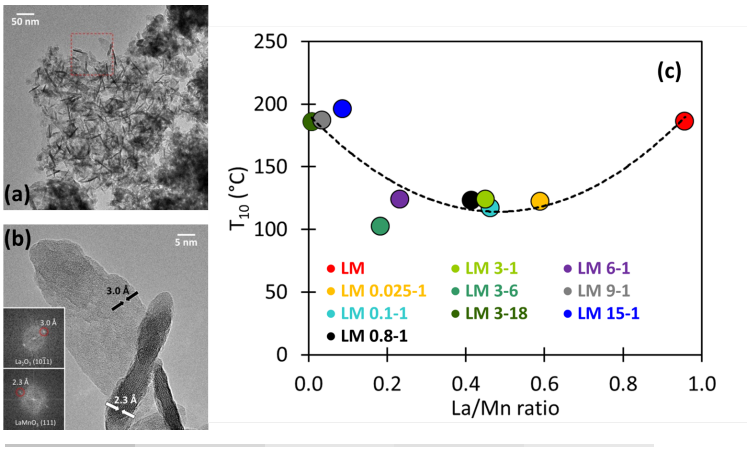
A. Toso[1], A. Felli[1], S. Colussi[1], M. Boaro[1], J. Llorca[2], C. Artner-Wallner[3], B. Truscott[3], A. Trovarelli[1]

[1]*Polytechnic Department of University of Udine, Via del Cotonificio 108 Udine (Italy)*
[2]*Universitat Politècnica de Catalunya, EEBE, Eduard Maristany 10-14, 08019, Barcelona, Spain*
[3]*Treibacher Industrie AG, Auer-von-Welsbach-Straße 1, Althofen (Austria)*
[*]*christine.artner-wallner@treibacher.com*

Keywords: $LaMnO_3$, acid treatment, CO oxidation, needle-like MnO_x

Introduction. The post treatment of $LaMnO_3$-based perovskites in acid solutions has received a considerable attention as interesting approach to improve the textural properties of the perovskite as well as its catalytic performance in VOC oxidation [1-2]. In this work, we studied in detail the effect of the acid concentration and time on the evolution of textural, morphological, redox and catalytic properties of acid modified $LaMnO_3$ in CO oxidation.

Experimental/methodology. 1 g of $LaMnO_3$ (LM, Treibacher Industrie AG) was treated in 240 ml of HNO_3 solution under stirring at room temperature. The solid, then, was washed with distilled water, centrifuged three times and dried overnight at 373 K. To evaluate the effect of the HNO_3 concentration, LM was treated in 0.025, 0.1, 0.8, 3, 6, 9 M and 15 M HNO_3 solutions for 1 hour. To study the effect of time, HNO_3 concentration was kept at 3 M, extending the treatment to 6 or 18 hours. The samples were named as follow "LM c-t", where c indicates the molar (M) HNO_3 concentration and t denotes the treatment time (h). The samples were characterized by means of ICP analysis, N_2 adsorption/desorption measurements, XRD, H_2-TPR, XPS, HRTEM and HAADF-STEM. CO oxidation test were carried out in 1% CO, 10% O_2 in N_2 at GHSV of around 135000 h^{-1}. Tha gas composition was monitired by on-line MKS 2030 FTIR multi gas analyzer.



Results and discussion. Depending on the strenght of the acid treatment, the catalyst composition significanly changes: La/Mn ratio gradually decreases from 0.96 on LM to 0.59-0.41 for the samples treated in 0.025-3 M solutions. On LM 3-6 and LM 6-1, La/Mn further decreases to 0.18 and 0.23, respectively, approaching zero on LM 3-18, 9-1 and 15-1. The BET surface area increases from 20.1 m^2/g on LM up to 166 m^2/g, with a corresponding increase of the pore volume from 0.13 cm^3/g up to 0.60 cm^3/g and larger pore size (30-700 Å), suggesting the formation of meso-macroporous network. In parallel, LM turns to a $MnO_x/LaMnO_3$-type catalysts with $LaMnO_3$ as main phase and traces of Mn_3O_4 (0.025-3 M) or MnO_x (MnO_2 and Mn_3O_4) (LM 3-6 and 6-1). Under severe acid conditions, $LaMnO_3$ structure collapses, resulting in pure MnO_x (MnO_2, Mn_3O_4 or Mn_2O_3). HRTEM analysis (Figure 1(a-b)) evidences the co-presence of perovskite and MnO_x in needle-shaped structures. Looking at Figure 1(c), $MnO_x/LaMnO_3$-type catalysts oxidized CO more efficiently, achieving 10% of CO conversion in the range of 102-126 °C, against 186°C on LM. The positive effect of the acid dissolution disappears when the catayst is pure MnO_x, denoting a positive effect from $LaMnO_3$-MnO_x interaction towards CO oxidation.

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Interface engineering of amorphous/crystalline catalysts employing metallic glasses and ceria for catalytic CO Oxidation

M. Shahim[1,2]*, L. Soler[2*], E. Pineda[1]

[1] *Institute of Energy Technologies and Departament de Física, Universitat Politècnica de Catalunya (UPC), Barcelona, Spain*

[2] *Institute of Energy Technologies and Department of Chemical Engineering, Universitat Politècnica de Catalunya (UPC), Barcelona, Spain*

**Corresponding Authors e-mail: maahin.mirzay@upc.edu; lluis.soler.turu@upc.edu*

Keywords: CO Oxidation, Metallic Glasses, Cerium dioxide, Mechanochemistry, Catalyst design

Introduction. The research of new catalysts with improved reaction performance and durability is of utmost importance for sustainable development and environmental protection. Among various solid-gas reactions, the oxidation of carbon monoxide (CO) is a key process in environmental care and the advancement of fuel cell technology. In particular, the preferential oxidation of carbon monoxide (COPrOx) in rich hydrogen (H_2) gas streams has been recognized as an effective route to purify H_2 produced by bioalcohol steam reforming reactions to extend the lifetime of the current electrocatalysts employed in low temperature fuel cells [1]. Metallic glasses have been identified as amorphous alloys with enhanced catalytic properties [2]. The lack of crystalline order introduces free volume in the material, thus producing an exponential increase in diffusivity of the chemical species. In addition, the highly defective structure increases the kinetics of many chemical reactions [3]. Here we will share new findings on metallic glass catalysts for CO oxidation and explore challenges in optimizing amorphous/crystalline interfaces for this reaction.

Experimental/methodology. We have produced **Cu-Zr-Al metallic glasses** by rapid quenching. The cooling rate during the quenching of the melted material is estimated to be 10^5 K s^{-1}, this ultra-fast cooling inhibits crystallization thus obtaining the metal in a disordered, glassy state. The absence of crystalline Bragg reflections indicates an amorphous structure of the alloy.

Results and discussion. The catalytic performance of amorphous $Cu_{47}Zr_{47}Al_6$ metallic glass-based samples was inspected by monitoring the CO conversion at different temperatures. The as synthesized $Cu_{47}Zr_{47}Al_6$ ribbons were ball milled to increase its specific surface area. As shown in Figure 1, 100% CO conversion was achieved at temperatures above 240°C when the metallic glass was ball milled with CeO_2 crystalline powder. Nevertheless, a lower catalytic efficiency was obtained when the pure counterparts (CeO_2 or the $Cu_{47}Zr_{47}Al_6$ metallic glass) were tested under identical experimental conditions. Our results demonstrate that the combination of amorphous Cu-based metallic glasses and crystalline CeO_2 display a remarkable catalytic activity and stability for CO oxidation.

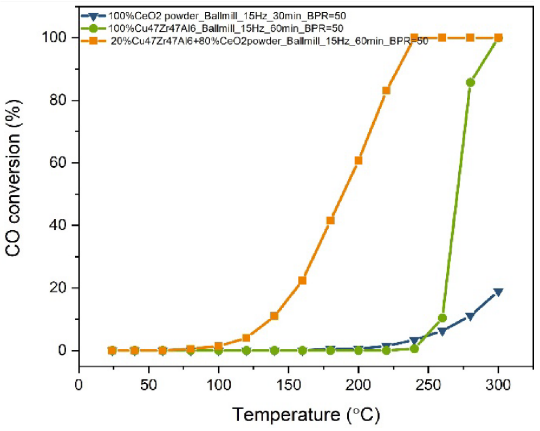

Figure SEQ Figure * ARABIC 1. CO conversion obtained during operation with a Cu-based metallic glass ($Cu_{47}Zr_{47}Al_6$) ball milled with CeO_2 as a model of amorphous phase catalyst for CO oxidation.

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Strong Solid Base site of N^{3-} beside vacancies in hexagonal-$BaTiO_{3-x}N_y$

M. Miyazaki[1*], H. Saito[1], K. Ogasawara[1], M. Kitano[1], H. Hosono[1]

[1] *Tokyo Institute of Technology, Yokohama, Japan*
[*] *miyazaki.m.ac@m.titech.ac.jp*

Keywords: Solid Base Catalyst, Oxynitride, Knoevenagel Condensation

Introduction. Solid base catalysts using oxide-based materials have been widely used for the application for C-C bond formation. [1] It is well known that oxides modified by alkali-metal compounds exhibited strong solid base profiles. [2] However, these typical catalysts suffer from a wide distribution of basic strength due to disordered alkali-metal doping and surface reconstruction during synthesis, it is not clear which structures exhibit strong basicity. Herein, we repoted the solid base catalyst with the site selective replacement of oxygen to nitrogen and vacancies in hexagonal-$BaTiO_{3-x}$. Increasing the electron density around N^{3-} site and the surface Lewis basicity promotes the catalytic activity for Knoevenagel condensation.

Experimental/methodology. A series of hexagonal-$BaTiO_{3-x}A_y$ (A = O, H, N) were prepared through the anion substitution of hydride in *h*-$BaTiO_{3-x}H_x$, prepared by direct reaction of BaH_2 and TiO_2 under H_2 at 800°C. *h*-$BaTiO_{3-x}N_y$ was prepared from *h*-$BaTiO_{3-x}H_x$ heated under a N_2 gas flow at 600°C. *h*-$BaTiO_{3-x}H_x$ was calcinated in air at 800°C to obtain *h*-$BaTiO_{3-x}$. Knoevenagel condensation reaction was conducted in a glass vial tube. Ethanol solution of methylene compounds, benzaldehyde, and *n*-dodecane was added to the catalysts in the vial under air at 70°C.

Results and discussion. The surface basic site of prepared materials are characterized via CO_2-TPD in Figure 1. All prepared catalysts exhibited weak basicity can be assined to CO_2 chemisorbed on the lattice oxygen near BaO- or TiO_2-terminated surface, and the strongest basic sites observed on *h*-$BaTiO_{3-x}N_y$. Based on the DFT calculation and XAFS measurements, the strong basicity on *h*-$BaTiO_{3-x}N_y$ was assign to the increase in the electron density of nitrogen caused by electron donation from adjacent vacancy site. To investigate the catalytic base activity, Knoevenagel condensation reaction between benzaldehyde and active nitrile compoinds with various pK_a was conducted. All of catalysts afforded in good yield of products with nitrile of low pK_a value, however, only *h*-$BaTiO_{3-x}N_y$ showed high catalytic activity for various nitlile up to pK_a = 23.8. Moreover, $BaTaO_2N$ and $LaTiO_2N$ without vacacies exhibited much lower yield than *h*-$BaTiO_{3-x}N_y$, indicating only N^{3-} sites adjacent to vacancies work as strong base sites in oxynitrides.

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Aluminum atoms organization in MFI ruled by synthesis procedure

V. Pashkova[1], P. Klein[1], M. Urbanova[1,2], J. Brus[2], L. Kobera[2], J. Dedecek[1], K. Mlekodaj[1*]
[1]*J. Heyrovský Institute of Physical Chemistry of the CAS v. v. i. Prague, Czech Republic*
[2]*Institute of Macromolecular Chemistry, The Czech Academy of Sciences, 162 06 Prague 6, Czech Republic*
[*]*E-mail: kingapatrycja.mlekodaj@jh-inst.cas.*

Keywords: Al-rich gel method, Al distribution, syntesis of zeolites, ZSM-5 zeolite.

Introduction. Control of Al organization in Si-rich zeolite matrices represents an important issue as it governs the catalytic performance of both acid and redox sites and represents one of the key parameters of the zeolite-based catalyst.[1,2] Isolated Al atoms, Al pairs (Al-O-$(Si\text{-}O)_2$-Al sequences in one zeolite ring), and close unpaired Al atoms (two close Al atoms located in different rings) were reported for silicon-rich zeolites.[1,2] ZSM-5 of MFI topology represents the most prominent Si-rich zeolite for catalytic applications. For this reason, synthesizing ZSM-5 materials with a maximized concentration of Al species, providing a high concentration of active sites suitable for selected processes, attracts significant attention. Isolated Al atoms and Al pairs were reported to be present in this matrix, and significant effort was spent to reach (semi)monomodal ZSM-5 matrices with prevailing single Al atoms or Al pairs using control of synthesis conditions (nature of Al and Si sources, presence of co-cations, etc.).[3,4] However, the preparation of ZSM-5 zeolites with a high fraction of Al pairs was limited to materials with rather higher framework Al content (Si/Al < 40). In this contribution, a new synthesis protocol enabling the preparation of Si-rich (Si/Al > 50) ZSM-5 zeolite matrices with over 80 % of Al atoms in Al pairs is reported. This method is based on the preparation of two gels (all-silica one and Al-rich one), which are aged and subsequently combined together before final crystallization under hydrothermal conditions.

Experimental/methodology. Sets of ZSM-5 zeolite synthesis gels of the same Si/Al were prepared. The gels varied in the procedure of preparation (sequence of mixing) while applied chemical reagents were the same (TEOS or TPAOH as SDA, $AlCl_3$ or $Al(NO_3)_3$ as Al source). The Al-rich gels of Si/Al = 4, 7, 7.5, 8.5, 12.5, 15, 30 and pure Si (Si/Al=∞) with SDA were prepared and combined to obtain final Si/Al=30 gels, which were subjected to crystallization under hydrothermal conditions (170 °C, 6 days, agitation). Crystalline products were characterized by XRD and SEM. Both synthesis gels and prepared zeolites after calcination were characterized using ^{27}Al and ^{29}Si MAS NMR spectroscopy, selected gels by ^{27}Al-^{27}Al double-quantum single-quantum MAS NMR spectroscopy. Al distribution in the zeolite product was analysed by Co(II) ions as a probe monitored by UV-Vis spectroscopy of dehydrated maximum Co(II) exchanged samples.[1,2]

Results and discussion. Zeolites prepared by mixing of Al-rich and pure silica gels exhibited significantly higher concentration of Al pairs in the framework (up to twice higher for syntheses using $AlCl_3$ and five-times higher for synthesis with $Al(NO_3)_3$ as Al source). This allowed preparing of ZSM-5 zeolite with Si//Al 30-60 and ~90 % of Al atoms in Al pairs. According multinuclear ss-NMR study, close Al atoms serving as precursor of Al-O-$(Si\text{-}O)_2$-Al sequences in zeolite are formed in the Al-rich gel with Si/Al < 9, and they are preserved after mixing of Al-rich gel with the all-silica one and transferred to the ZSM-5 framework. The suggested here mechanism of transferring larger Al-O-Si-O-Al sequences into ZSM-5 product can be considered in analogy to the one already proved for SSZ-13 zeolite synthesized using various zeolites as Al and Si sources.[5]

The synthesis strategy to maximize the concentration of Al pairs in silicon-rich matrices is reported. This strategy can be suggested to be not limited by the structure directing agent or Si and Al sources used in the synthesis gel preparation. Thus, it represents a very promising tool for tuning Al distribution in various silicon-rich zeolite matrices.

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Syngas production by CO_2 reforming of methane on $Ni/LaAlO_3$ perovskite based catalysts with improved textural properties

H.J. Muñoz, S.A. Korili, A. Gil*

INAMAT^2, Science Department, Los Acebos Building, Public University of Navarre, Campus of Arrosadia, Pamplona, Spain

**andoni@unavarra.es*

Keywords: Perovskite, lanthanum aluminate, sol-gel, methane, and carbon dioxide.

Introduction. Dry reforming of methane (DRM) has received considerable attention because it can reduce greenhouse gas emissions (CO_2 and CH_4) while converting them into valuable syngas (H_2 and CO) [1]. The $Ni/LaAlO_3$ catalysts are considered promising materials for the application of this technology. However, there are several challenges when using Ni-based catalysts such as sintering of the active phase and carbon deposition on the catalyst surface due to the high temperatures used in the DRM reaction [2]. Therefore, the textural properties of the catalytic support play an important role [3], for this reason, the present study reports for the first time a simple strategy to prepare the pure perovskite phase of $LaAlO_3$ with a high specific surface area as catalytic support. This study demonstrates that the textural, structural, and catalytic properties can be modulated by optimizing the solvothermal treatment time.

Experimental/methodology. The perovskite supports were obtained after the reaction between an organic ligand and the precursor salts of Al and La in ethanol at 120 °C at several times (t = 4, 6, 12 and 24 h) (*MOX-(t)-Al-La*), then these were calcined at 750 °C (*MOX-(t)-Al-La-750*). A material called MOX-Ex-Al-La-750 was also prepared by the addition of La to the MOG-Al-100 gel precursor and finally, the reference material was synthesized by using the citrate sol-gel method (C-Al-La-750), both materials were calcined at 750 °C. The catalysts were prepared by incipient impregnation with 10 wt.% of Ni and these were denoted *as MOX-(t)-$LaAlO_3$-Ni* (t = 12 and 24 h) or C-$LaAlO_3$-Ni. The catalysts were evaluated in the DRM reaction for 20 h at 700 °C.

Results and discussion. Among the MOGs evaluated, the *MOX-(t)-Al-La* (t = 12 and 24 h) had the highest specific surface areas and showed sponge-like porous structures. The X-ray diffraction results of the samples calcined and solvo-thermally treated materials for t = 6, 12, and 24 h (*MOX-(t)-Al-La-750*) showed diffraction peaks of the crystallographic planes coincided with the theoretical pattern of lanthanum aluminate (JCPDS card No. 96-220-6577) without the presence of impurities such as La_2O_3. It should be noted that the *MOX-(t)-Al-La* (t = 12 and 24 h) materials maintained the mesoporous characteristics of the La-Al-MOG precursors with high specific surface areas, these were up to three times higher than the reference material, the aforementioned due to the low calcination temperature necessary for crystallization. The properties obtained on perovskite-type supports of solvo-thermally treated materials for 12 and 24 h allowed a high dispersion of the active sites of Ni. However MOX-(12h)-$LaAlO_3$-Ni showed the best catalytic performance with an H_2/CO ratio close to 1, CO_2 conversion of 80% and methane conversion of 75% after 20 h of reaction, which was superior compared to reference catalyst and catalysts based on lanthanum aluminate previously reported in the literature. The explanations for this catalytic behavior in the DRM reaction were derived from the following physicochemical properties: *(i)* improved textural properties of the support; *(ii)* the presence of α- and β_1-Ni species; *(iii)* NiO species with a strong oxide/support interaction and *(iv)* resistance to the formation of a dense network of interconnected carbon filaments.

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Size dependence of niobium oxide clusters for base catalysis

H. Nagakari[1], S.Kikkawa[1], N.Nakatani[1], S.Yamazoe[1,2*]

[1] *Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Tokyo 192-0397, Japan.*

[2] *Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), Tokyo 102-0076, Japan.*

[*] *Yamazoe@tmu.ac.jp*

Keywords: base catalyst, polyoxometalate, polyoxoniobate

Introduction. Acid and base catalysts are essential for industrial processes in petroleum chemistry and biomass conversion. Group V metal oxides such as Nb_2O_5 are generally known to act as acid catalysts.[1)] On the other hand, we recently reported that niobium oxide clusters(PONb), exhibit Brønsted and Lewis base catalysis for Knoevenagel condensation (KC) and CO_2 fixation reactions, respectively[2)]. The Brønsted base properties of $[Nb_6O_{19}]^{8-}$came from highly negative charges of surface oxygen, as calculated by DFT calculations. However, the origin of the strong basicity of niobium oxide clusters is not fully understood yet. In this study, we synthesized a series of niobium oxide clusters with different sizes, such as $[Nb_6O_{19}]^{8-}$ [2)], $[Nb_{10}O_{28}]^{6-}$ [3)], and $[Nb_{20}O_{54}]^{8-}$ [4)], with the same counter cation of tetrabutylammonium ion (TBA+) by using a microwave-assisted hydrothermal synthesis and applied them to KC reaction to evaluate their basicity (Fig. 1).

Fig. 1 Structure of Nb6, Nb10, Nb20. NBO charges of surface oxygen.

Experimental/methodology. The TBA salts of $[Nb_6O_{19}]^{8-}$(Nb6) and $[Nb_{10}O_{28}]^{6-}$(Nb10)were prepared by a microwave-assisted hydrothermal synthesis, which $Nb_2O_5{\cdot}nH_2O$ were treated in aquaeous solution of TBAOH with the optimized heating conditions. The TBA salts of $[Nb_{20}O_{54}]^{8-}$(Nb20) were obtained by precipitation filtration collection of TBA salts of Nb10 dissolved in dichloromethane in ethyl acetate. Base catalytic properties were evaluated by KC reactions, where nitrile compounds of different pK_a (16.0, 21.9, 23.8) were reacted with benzaldehyde (BA) in DMSO at 70°C for 24 h under N_2 atmosphere. DFT calculations (B3LYP functional) were performed using Gaussian16 with the basis functions of Lanl2dz for Nb and 6-31++G** for O and H.

Results and discussion. Elemental analysis, ESI-MS and ATR-IR revealed that clusters of the target composition could be synthesized**.** Fig. 2 shows the BA conversion at 70°C in KC reactions using substrates having various pKa. As for the substrates of pKa of 21.9 and 23.8, Nb6 showed high activities, followed by Nb10. Nb20. The catalytic activity of Nb20 for KC reaction with the substrate having pKa = 16.0 was higher than that of bulk $Nb_2O_5{\cdot}nH_2O$, although Nb20 hardly worked as a base catalyst for KC reactions above pKa of 21.9. The order in base catalytic activity corresponded to that in their negative charges of surface oxygens which are considered to be the basic active sites. We also discuss the relationship between the base strength and KC activities by using DFT calculations .

Fig. 2 BA conversion in KC reactions using substrates having different pKa.

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Surface Dynamics for Generation of Metal Active Sites for Ammonia Synthesis under Mild Conditions

Katsutoshi Nagaoka,[1,*] Katsutoshi Sato,[1] Shin-ichiro Miyahara,[1] Koji Inazu[2]

[1]*Graduate School of Engineering, Nagoya University, Nagoya, 464-8603, Japan*
[2] *National Institute of Technology, Numazu College, Numazu, Shizuoka 410-8501, Japan*
[*] *nagaoka.katsutoshi@material.nagoya-u.ac.jp*

Keywords: Carbon-neutral society, Energy (Hydrogen) carrier, Green ammonia

Introduction. Ammonia has gained a lot of attentions as a potential energy (H_2) carrier for utilizing renewable energy. To construct such a system, there is a strong need to develop an innovative catalytic process for ammonia synthesis. Ammonia is currently produced by the Haber-Bosch process and is manufactured at high temperature and high pressure (>450 °C and >20 MPa) over an iron-based catalyst. It is expected to develop a catalyst that produces ammonia efficiently under mild reaction conditions (300-400 °C, <10 MPa) that can reduce energy consumption in the green ammonia synthesis process. We have reported that Ru catalysts supported on composite rare earth oxides such as $La_{0.5}Ce_{0.5}O_{0.75}$ [1] and $Ba_{0.1}La_{0.45}Ce_{0.45}O_{1.68}$ [2] exhibit high NH_3 synthesis rates under mild conditions (300 - 400 °C, 1.0 MPa) when reduced at an unusually high temperature of 650 °C. These catalysts are easy to prepare, stable in air, and suitable for practical use. By further applying these concepts to inexpensive Co catalysts, we have succeeded in discovering Co/Ba/MgO [3] and Co/Ba/La_2O_3 [4] catalysts. Especially, Co/Ba/MgO pre-reduced at 700 °C shows higher NH_3 synthesis rate than benchmark Ru catalysts at 350 °C and 3 MPa. In this contribution, we will address the performance of the Co/Ba/MgO and formation mechanism of active site, i.e. Co@BaO core-shell structure, during pre-reduction.

Experimental/methodology. Oxide-supported metal catalysts were prepared by wet impregnation. Co and Ru loadings were 20 and 5 wt%, respectively. The NH_3 synthesis rate was evaluated using a conventional flow system.

Results and discussion. Fig. 1 represents pressure dependence of NH_3 synthesis rate at 350 °C. At 0.1 MPa, the Co/Ba/MgO_700°Cred (xxx°Cred means that the catalyst was pre-reduced at xxx °C) catalyst exhibited a lower NH_3 synthesis rate than the two benchmark Ru catalysts. However, the NH_3 synthesis rates of these Ru catalysts did not rise much even when the reaction pressure was increased to 3.0 MPa due to strong hydrogen adsorption property of Ru, so-called hydrogen poisoning. By contrast, the NH_3 synthesis rate of Co/Ba/MgO_700°Cred increased drastically when the reaction pressure was increased to 3.0 MPa, and at this pressure the synthesis rate was much higher than those of the Ru catalysts. The reaction order for H_2 for the Co catalyst is 0.37, revealing that this catalyst is not poisoned by H_2. We have shown that pre-reduction of the catalyst at high temperature leads to surface rearrangement, forming BaO-encapsulated Co nanoparticles (Co@BaO) on the MgO surface, with all available Co sites on the surface adjacent to BaO nanofractions, and that such a structure promotes the dissociation of N≡N bond, the rate-determining step in ammonia synthesis. The formation of this unique structure is thought to consist of the reduction of oxidized Co to metallic Co, decomposition of $BaCO_3$ to BaO via $Ba(OH)_2$, and migration of BaO and Co nanoparticles.

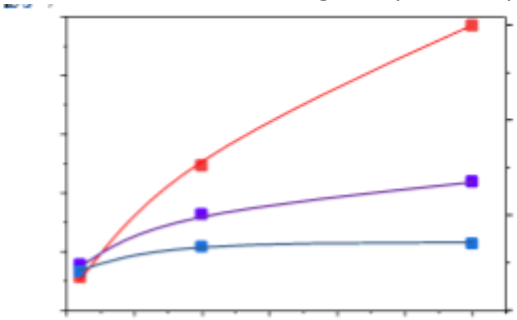

Fig. 1. Effect of pressure on the rate of NH_3 synthesis at 350 °C.

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Stability of supported catalytically active liquid metal solutions (SCALMS) catalysts in high temperature reactions

Sharanya Nair[1*], Nicola Taccardi[1], Marco Haumann[1], Peter Wasserscheid[1,2]

[1]*Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Lehrstuhl für Chemische Reaktionstechnik (CRT), Erlangen, Germany*
[2]*Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), Forschungszentrum Jülich, Erlangen, Germany*
[*]*Corresponding Author's E-mail address: sharanya.nair@fau.de*

Keywords: Supported catalytically active liquid metal solutions (SCALMS), alloy, dynamic liquid interface, catalyst poisoning, dehydrogenation

Supported catalytically active liquid metal solutions (SCALMS) catalysts consist of small amounts of catalytically active metal dissolved in a low melting point liquid metal. The resulting alloy is deposited on a porous support. The catalyst composition plays an important role in determining whether the metal alloy will be present in liquid phase under reaction conditions. The liquid nature leads to highly dynamic interfaces.[1] Various bimetallic alloys with Ga as the liquid metal matrix have been tested as SCALMS for different chemical reactions, namely GaPd for n-butane dehydrogenation [1], GaRh for propane dehydrogenation [2], GaPt for methylcyclohexane dehydrogenation [3], and GaNi for ethylene oligomerization reaction.[4] The influence of support material has also been studied for GaPt based SCALMS.[5] All these studies indicated towards the high specific activity of SCALMS catalysts.

For industrial catalytic processes, deactivation via catalyst poisoning and coking is a major issue. Feedstock purification and commercial catalyst regeneration processes have contributed to significant expenses. Pre-liminary studies based on SCALMS catalysts indicate towards the role of the unique nature of the atomically dispersed active metal sites at the liquid interface in altering the coking behaviour. We extend our investigation to poisoning studies where we will deliberately expose the GaPt based SCALMS catalyst to typical catalyst poisons **(Fig. 1)** i.e., CO and H_2S.[6] The objective of our work is to study the influence of various factors on further enhancing the performance of the SCALMS catalysts under harsh reaction conditions. These factors include the catalyst composition, pre-treatment conditions, duration of exposure to poison etc. We choose isobutane dehydrogenation reaction as it is a clean reaction with few by-products thereby ideal to understand the effect of these factors on the SCALMS catalyst performance.

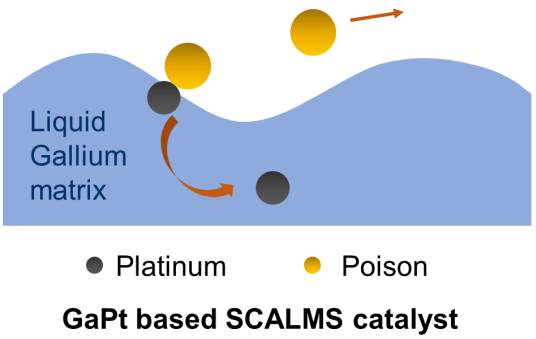

Figure 1: Schematic showing the influence of catalyst poison on GaPt based SCALMS catalyst performance.

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Study on the catalytic active species for partial oxidation of CH_4 over Fe-containing zeolite

K. Nakamura[1], P. Xiao[1], J. N. Kondo[1] and T. Yokoi[1*]

[1]*Tokyo Institute of Technology, Yokohama, Japan*
[*] *yokoi@cat.res.titech.ac.jp*

Keywords: CHA, Zeolite, Methane conversion,

Introduction. Direct conversion of methane to methanol (MTM) reaction is a hot topic. We have investigated on the zeolite-based catalytic process that can produce lower hydrocarbons from methane *via* methanol.[1] In this process, copper-containing CHA-type zeolite with high Al content is applied as a catalyst; abundant acid sites can work as ion-exchange site for capturing Cu species, which produce methanol, and remaining acid site enhance the conversion of the methanol produced into lower hydrocarbons. Recently, it has been well-recognized that the control of Al atoms in the framework is particularly important for catalytic performance. We have reported that the Al distribution in zeolite framework of CHA-type zeolite can be controlled by changing the starting materials.[2] In this study, we prepared Fe-exchanged CHA-type aluminosilicate zeolites with different Al distributions. The effect of framework Al distribution in CHA-type zeolites on the ion-exchange properties and methane conversion properties was investigated.

Experimental/methodology. The CHA-aluminosilicate zeolite was synthesized under organic-directing agents (OSDA)-free method by hydrothermal synthesis. In addition to amorphous silica and alumina, FAU-type zeolite (Si/Al=15) was applied as the starting material; the uses of amorphous and FAU were named CHA-Am and CHA-FAU, respectively. Fe species were introduced into the NH_4^+ form CHA by ion-exchange method. The obtained samples were characterized by XRD, ICP-AES, ^{29}Si, ^{27}Al MAS NMR, UV-vis spectrum analysis, and FT-IR. Catalytic oxidative methane conversion reaction was carried out in a continuous flow reactor under atmospheric pressure. The reaction was carried out at 350 °C with a mixture of CH_4, N_2O, and H_2O (P_{CH4} = 0.08 atm, P_{N2O} = 0.08 atm, P_{H2O} = 0.08 atm, P_{Ar} = balance) at 25 mL min^{-1}.

Result and discussion. The XRD patterns of all the products showed a typical CHA-type structure. The CHA structure was retained even after the Fe loading. The ^{29}Si MAS NMR spectra of the NH_4^+ form CHA-Am and CHA-FAU samples indicated that, based on the deconvolution of the all the peaks, the proportion of $Q^4(1Al)$ species in CHA-FAU was significantly higher than that in CHA-Am, indicating that the Al distribution is different depending on the starting material ($Q^4(nAl) = (Si(OSi)_{4-n}(OAl)_n)$). The ICP-AES analysis results showed that the Si/Al ratios of Fe/CHA-Am and Fe/CHA-FAU were found to be 5.5 and 4.6, respectively and that Fe content was nearly equal in Fe/CHA-Am (Fe/Al = 0.10, 1.48 wt%) and Fe/CHA-FAU (Fe/Al = 0.10, 1.65 wt%). Figure 1 shows the catalytic performance of Fe/CHA-Am and Fe/CHA-FAU. Note that there was marked difference in total yield of hydrocarbons between Fe/CHA-Am and Fe/CHA-FAU; Fe/CHA-FAU (about 5 %) gave twice as high as Fe/CHA-Am. The difference in reactivity would be caused by the Al distribution in the framework. In this presentation, we will discuss the effects of the Al distribution on Fe ion state and reaction results based on FT-IR.

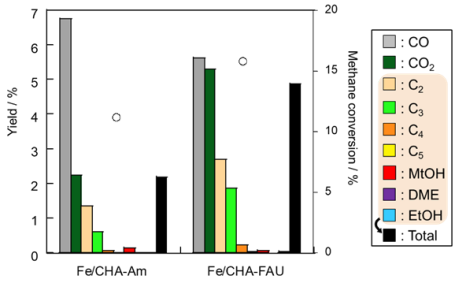

Figure 1. Oxidative conversion of CH_4 with N_2O over CHA zeolite catalysts. (○) Conversion of CH_4, the bars represent the yields to CH_3OH, DME, C_2H_5OH, hydrocarbons (C2~C5), CO and CO_2, respectively. Black bars show the total yield of hydrocarbons (C2~C5, methanol, DME, ethanol).

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Development of Supported Gold Cluster Catalysts Utilizing Layered Double Hydroxide (LDH) Nanoparticles

A. Nakayama[1], A. Yoshida[1], T. Honma[2], N. Sakaguchi[3], A. Taketoshi[4], T. Fujita[5], T. Murayama[1], T. Shimada[1], S. Takagi[1], T. Ishida[1*]

[1]*Department of Applied Chemistry for Environment, Tokyo Metropolitan University, Tokyo, Japan*
[2]*Japan Synchrotron Radiation Research Institute (JASRI), Hyogo, Japan*
[3]*Center for Advanced Research of Energy and Materials, Hokkaido University, Hokkaido, Japan*
[4]*Department of Advanced Materials Chemistry, Yokohama National University, Kanagawa, Japan*
[5]*Department of Applied Chemistry, Tokyo University of Technology, Tokyo, Japan*
[*]*Corresponding Author: tamao@tmu.ac.jp (T. Ishida)*

Keywords: Au clusters, layered double hydroxides, alcohol oxidation

Introduction. Au catalysts have attracted much attention due to their unique catalytic performance. Because the catalytic activity of Au strongly depends on the size of Au, minimization of Au particle size has been intensively studied. However, deposition of Au clusters and single atoms is still challenging and there is a still room for improvement; such as low Au loading and/or limited types of supports (e.g., CeO_2, Co_3O_4, and NiO). Layered double hydroxides (LDHs) are composed of M(II) hydroxides in which M(III) is partly replaced with M(II). Zhang et al. reported that the lateral planes of LDHs could stabilize Au as clusters more efficiently than the basal planes.[1] Therefore, LDH nanoparticles (NPs) having abundant edges are expected to be a suitable support for small Au particles. Here, we aimed at deposition of Au single atoms and clusters using Mg-Al LDH NPs, which are supported on SiO_2. The changes of electronic states and size of Au during reduction of Au(III) was analyzed by in-situ XAFS, and the catalytic activity was evaluated by benzyl alcohol oxidation.

Experimental. Mg-Al LDH NPs were prepared according to the literature.[2] Then, aqueous solution of $HAuCl_4$ (Au 2 wt%) was added to a dispersion of LDH NPs, and the mixture was stirred at 0 °C for 4 h. Subsequently, SiO_2 was added and stirred at 0 °C for another 1 h to obtain 0.8 wt% Au(III)@LDH/SiO_2. The obtained Au(III)@LDH/SiO_2 was treated in 10 vol% H_2/N_2 (50 mL min^{-1}) at 120 °C for 2 h to obtain Au(0)@LDH/SiO_2, or in air at 400 °C for 4 h to transform LDH into mixed metal oxide (MMO) to give Au(0)@MMO/SiO_2. The prepared catalysts were analyzed by in-situ X-ray absorption fine structure (XAFS) and transmission electron microscopy (TEM). For the catalytic reaction, benzyl alcohol (20 mmol), tridecane (30 mg), and a catalyst (Au 0.001 mol%) were placed in an autoclave. The reaction was carried out under pressurized O_2 (2.0 MPa) at 150 °C for 1 h. The conversions and yields were analyzed by GC.

Results and discussion. In-situ XAFS measurements of 0.8 wt% Au(III)@LDH/SiO_2 was performed under H_2 flow from room temperature to 120 °C. Au(III) was gradually reduced to Au(0) (Fig. 1a), but the peak corresponding to Au-Au bonds were not observed (Fig. 1b) suggesting the formation of Au single atoms. HRTEM revealed that Au single-atoms were observed together with Au clusters (1.2±0.7 nm) on Au(0)@LDH/SiO_2. Although Au single-atoms were disappeared on Au(0)@MMO/SiO_2, the diameter of Au was still 1.2±0.5 nm. Au(0)@MMO/SiO_2 showed superior activity for benzyl alcohol oxidation (TOF: 52,071 h^{-1}, selectivity: 81.0 %) to Au(0)@LDH/SiO_2 (TOF: 3,117 h^{-1}, selectivity: 99.6 %). Although Au was aggregated on Au(0)@LDH/SiO_2, the size of Au for Au(0)@MMO/SiO_2 was maintained. The high durability Au(0)@MMO/SiO_2 led to its high activity.

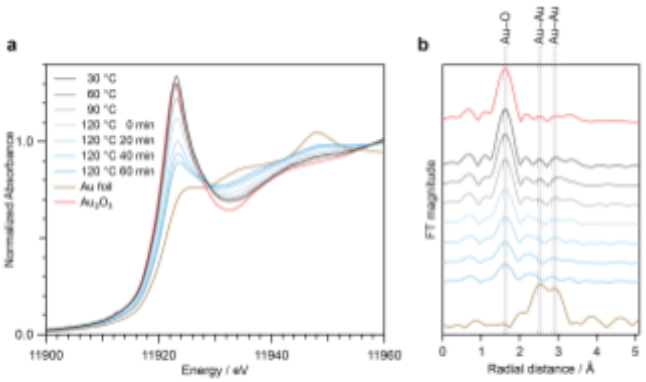

Fig. 1 Au L_3-edge in-situ XANES spectra (a) and radial structure functions (b) of Au(III)@LDH/SiO_2 during heat treatment in the flow of 10 vol% H_2/N_2.

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Reduction of nitroarenes to anilines in water solution catalyzed by Cu/SteelSlags new material

D. Nefedova*, M. Mali, G. Romanazzi, P. Mastrorilli, M. M. Dell'Anna

Politecnico di Bari, 70126 Bari, Italy
**darya.nefedova@poliba.it*

Keywords: Steel slags, copper catalyst, nitroarenes reduction

Introduction. The chemical reduction of nitroarenes to form anilines is a crucial step in the synthesis of a variety of industrially important compounds such as drugs, dyes, and materials.[1] Copper-based catalysts have gained significant attention in recent years for promoting this reaction as they can activate hydrogen molecules and facilitate their addition to the nitro group.[2] This enhances the efficiency of the process and can result in higher yields of the desired anilines. Conversely, basic steel slags are produced during the steelmaking process and contain a variety of metals such as iron, calcium, silicon, magnesium, and aluminium.[3] Their unique characteristics enable steel slags to act as catalysts for some chemical reactions. Thus, the use of copper catalyst supported on steel slags matrix for the nitroarene reaction could be promising in the development of new and more efficient synthetic methods for the synthesis of anilines and other nitrogen-containing compounds.

Experimental/methodology. The precursor of Cu/SteelSlags catalyst was obtained by mixing 9,4 mmol of copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) and 3.4 g of steel slags in 200 ml of H_2O for 2 hours, followed by separation of the solid fraction by centrifugation and drying at 80°C during 12h. The transformation of copper oxide into an active metal form occurred under reaction reductive conditions.

The reductive reactions of nitroarenes to corresponding anilines were carried out at room tempreture in a round flask equipped with a magnetic stirrer and a gas bubbler in the presence of 0.5 mmol of nitroarene, 3.0 mmol of $NaBH_4$, 50.0 mg of Cu/SteelSlags catalyst precursor and 5.0 ml of H_2O.

Recyclability test was carried out at room tempreture in round flask equipped with a magnetic stirrer and a gas bubbler in the presence of 2.0 mmol of nitrobenzene, 6.0 mmol of $NaBH_4$, 200 mg of Cu/SteelSlags catalyst precursor and 10 ml of H_2O. After each cycle of reaction the catalyst was washed with distilled water and methanol, and dried at 80°C and used for a subsequent run.

Results and discussion. The synthesized catalyst was tested in the reduction of different nitroarenes (table 1). The reduction of the active component from Cu^{2+} to Cu^0 occurred *in-situ* under reaction conditions, as evidenced by the change in the color of the catalyst from blue-gray to black. The recyclability test showed a consistently high yield of aniline over 4 cycles.

Table 1. Activity of Cu/SteelSlags catalyst in reactions of nitroarenes reduction

Entry	Substrate	Product	Time, h	Yield, %
1	Nitrobenzene	Aniline	2	>99
2	4-Fluoronitrobenzene	4-Fluoroaniline	2	>99
3	4-Cloronitrobenzene	4-Cloroaniline	4	>99
4	4-Bromonitrobenzene	4-Bromoaniline	4	>99
6	2-Nitrotoluene	2-methylaniline	1	>99
7	3-Nitrotoluene	3-methylaniline	2	>99
8	4-Nitrotoluene	4-methylaniline	2	>99
9	3-Nitroanisole	3-anisidine	2	>99

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Study of the effect of the La/Ce ratio of fluorite catalysts in the oxidative coupling of methane

Y. L. de Lima[1], G. L. Catuzo[1], D. D. Petrolini[2], E. M. Assaf[1]*

[1]*University of São Paulo, São Carlos, Brazil*
[2]*Tufts University, Medford, United States*
eassaf@iqsc.usp.br

Introduction. The oxidative coupling of methane is a very promising way of mitigating the methane concentration in the atmosphere, and at the same time transforming this pollutant into added-value products. In this work, we synthesized La-Ce fluorite-type catalysts with different La/Ce ratios by the surfactant-assisted hydrothermal method. Here, we aim to investigate the catalysts' physicochemical characteristics and correlate them with the catalytic properties in this reaction.

Experimental/methodology. In a typical synthesis, lanthanum and cerium nitrates were used as La and Ce sources, respectively. Polyvinylpyrrolidone was the surfactant and NH_4OH was the precipitant. The hydrothermal synthesis was carried out at 180 °C, for 24 h. Samples were washed and calcinated at 850 ºC. The reactions were performed at 550, 650, 750, and 850 °C, in a continuous-flow fixed-reactor (30:6:24 mL/min for CH_4:O_2:N_2), under a GHSV of 18,000 mL h^{-1} g^{-1}. The samples, with nominal La/Ce ratios of 0.075, 0.333, 1, and 3, were named LaCe-0.075, LaCe-0.333, LaCe-1, and LaCe-3, respectively.

Results and discussion. From the XRD patterns (Fig. 1a), the fluorite phase (marked as a grey *) and the La_2O_3 phase (marked as the red "X"), formed with increasing La content, were both identified. Additionally, new peaks (marked as yellow *) emerged with increasing La/Ce ratio, evidencing the formation of solid solutions between La and Ce atoms. From TPD-CO_2 (Fig. 1b), the basic sites concentration present on the surface of the catalysts are according to the following order: LaCe-0.075 < LaCe-0.333 < LaCe-1 < LaCe-3.

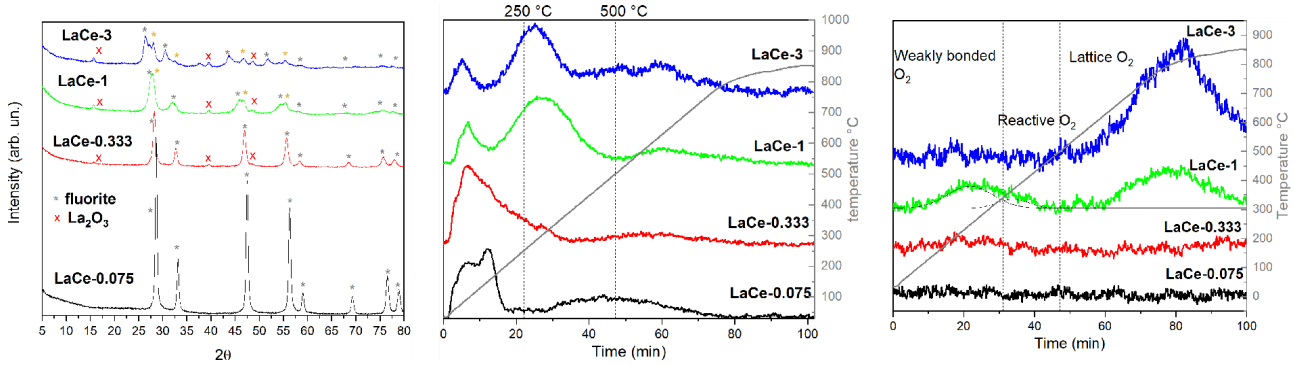

Figure 1: (a) X-ray diffraction patterns; (b) TPD-CO_2 and (c) TPD-O_2 curves of the calcinated samples.

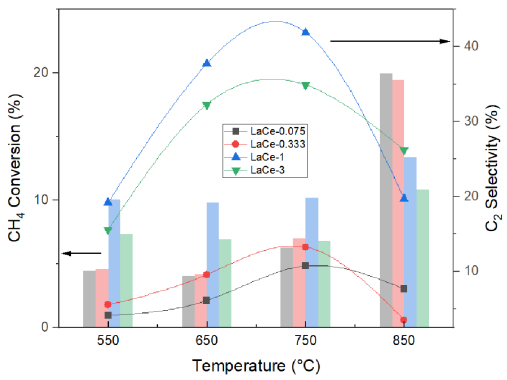

Figure 2: CH_4 conversion and C_2 selectivity for La-Ce catalysts.

However, the LaCe-1 catalyst showed the highest amount of moderate basic sites (between 250 and 500 °C), associated with a good C_2 selectivity for this reaction. Furthermore, this sample presented a higher amount of reactive O_2 for the AOM, as can be seen in Fig. 1c, from TPD-O_2. Fig. 2 depicts the methane conversion and selectivities to C_2 compounds (ethane and ethylene) as a function of temperature. The by-products, CO and CO_2, were omitted. The LaCe-1 catalyst presented the highest CH_4 conversion and C_2 selectivity, except at 850 °C. Such sample presented higher amounts of moderate basic sites and reactive oxygen, both properties notably known for selective conversion to C_2 compounds [1].

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Palladium Phosphide Catalysts for the Wacker-Tsuji-Oxidation of Alkenes

A. Neyyathala[1], F. Flecken[1] , JProf. S. Hanf[1]*

[1]*Karlsruhe Institute of Technology, Karlsruhe, Germany*

** schirin.hanf@kit.edu*

Keywords: Wacker-Tsuji-oxidation, alkenes, palladium phosphide, supported catalysts, heterogeneous-catalysis

Introduction.

The oxidation of alkenes to methyl ketones is an industrially important chemical reaction and it is used in the manufacturing of a wide spectrum of products, such as fine chemicals, organic intermediates and agrochemicals.[1,2] Therefore, the development of active, reusable and easily separatable solid state catalysts for oxidation catalysis has great significance in an industrial context. Consequently in this work, a supported palladium phosphide catalyst was synthesized and applied in the Wacker-Tsuji oxidation of styrene. The goal was hereby to reduce the noble metal content with respect to a sustainable use of metal resources, while maintaining or even enhancing the catalytic activity through the incorporation of phosphorus.

Experimental/methodology.

Silica supported palladium phosphide (Pd_3P/SiO_2) with 10 wt.% Pd loading was synthesized using an impregnation method followed by thermal treatment in hydrogen. The synthesized catalyst was characterized by PXRD, XPS, SEM-EDX, ICP-AES, and FTIR. Catalytic tests were performed in batch reactors, considering four reaction systems with variations in co-catalysts and oxidants, followed by an assessment of reaction time and temperature dependency. Recovery tests and filtration tests were performed to access the reusability of catalyst and heterogeneous nature of the catalytic system.

Results and discussion.

PXRD analysis of the synthesized catalyst confirmed the formation of the Pd_3P phase on SiO_2 and XPS unveiled zero valent surface Pd species. Superior catalytic performance is observed for Pd_3P in comparison to a purely Pd-based supported catalyst, which shall be attributed to the more defined active sites of Pd_3P in comparison to pure Pd.[3]

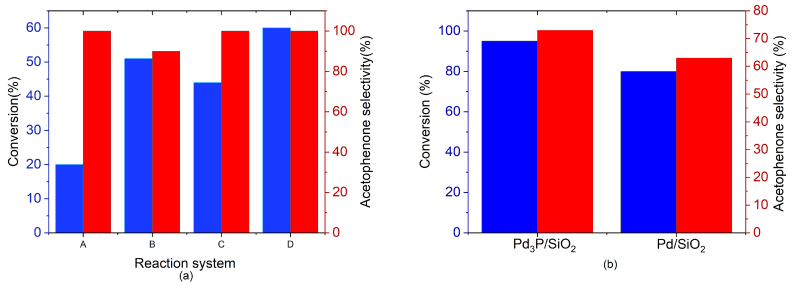

Figure 1 a) Comparison of different reaction systems: A: styrene, CuCl, THF, H_2O, O_2; B: styrene, $CuCl_2$, THF, H_2O, O_2; C: styrene, 30 % H_2O_2, 70 % H_2SO_4, MeCN and D: styrene, 30 % H_2O_2, acetic acid, H_2O. Test conducted at 50°C for 6h with Pd_3P/SiO_2 catalyst. b) Performance comparison of Pd_3P and Pd in reaction system B at 50°C for 16h.

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Photo-induced Active Lewis Acid-base Pairs in Metal-Organic Framework for H_2 Activation

Bryan Kit Yue Ng[1], Xin-Ping Wu[2], Shik Chi Edman Tsang[1*]

[1]*Department of Chemistry, University of Oxford, United Kingdom*
[2]*Key Laboratory for Advance Materials, East China University of Science and Technology, China*
**edman.tsang@chem.ox.ac.uk*

Keywords: Metal-organic Frameworks (MOFs), hydrogen activation, photocatalysis

Introduction. The establishment of active sites as Frustrated Lewis Pair (FLP) has recently attracted much attention from homogeneous to heterogeneous systems in the field of catalysis[1]. Their unquenched reactivity of Lewis acid and base pairs in close proximity that are unable to form stable adducts has shown to be able to activate small molecules such as dihydrogen heterolytically.

Experimental/methodology. Herein, by utilising the chemical stability and wide tuneability of UiO series metal-organic frameworks, we demonstrate that grafted Ru metal-organic framework-based catalysts prepared via N-containing linkers are rather catalytically inactive for H2 activation despite the application of elevated temperatures.

Results and discussion. However, upon light illumination, charge polarization of anchored Ru bipyridine complex can form transient Lewis acid-base pair, Ru^{+}-N^{-} via metal-to-ligand charge transfer, and this is confirmed by time-dependent density functional theory (TDDFT) calculations to carry out effective H2-D2 exchange. FTIR and 2-D NMR endorse the formation of such reactive intermediate(s) upon light irradiation.

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Bridging the Gap between Molecular and Solid Catalysts: Nanoporous Phosphine-Based Macroligands for the Activation of CO_2

Arne Nisters[1], Marcus Rose[1*]

[1] *Chemical Technology II, Technische Universität Darmstadt, Darmstadt, Germany*
[*] *marcus.rose@tu-darmstadt.de*

Keywords: CO_2 hydrogenation, phosphine-based macroligands, hyper-cross-linked polymers

Introduction: In the last two decades, the hydrogenation of CO_2 as C1 building block has attracted increasing attention. Due to its high stability, the development of catalysts plays a crucial role and was addressed by various studies, leading to a large variety of active homogeneous catalysts.[1] Despite their excellent catalytic performance, difficulties occur in the catalyst recyclability and the product separation. Therefore, the heterogenization of the molecular species has evolved with great opportunities in catalyst development. In recent years, porous organic polymers, which combine a high accessibility of functional moieties with an adjustable topology, were subject of several investigations.[2] Among this class of materials, polyphosphines with permanent porosity have been reported.[3,4] In our work, we developed novel phosphine-based macroligands for the immobilization of molecular ruthenium centers. The versatility of the topological design and the coordination sphere enabled a systematic investigation about the influence of the macroligand on the catalytic reactivity of the metal species.[5]

Experimental/Methodology: The versatile macroligands, which refer to the class of hyper-crosslinked polymers, are synthesized by the external knitting of phosphine units. Bifunctional crosslinkers such as α,α′-dibromo-*p*-xylene, 4,4′-bis(chloromethyl)-1,1′-biphenyl or dimethoxymethane connect the phosphines via Friedel-Craft-alkylations in the presence of the Lewis catalyst $AlCl_3$. These obtained insoluble networks are afterwards impregnated with ruthenium precursors by ligand exchange from solution. The thus formed catalysts are evaluated in the aqueous phase hydrogenation reaction of CO_2 to formic acid. The base-mediated catalysis is conducted in batch autoclaves at 110 °C and an elevated pressure of 60 bar.

Results and Discussion: The network formation and the incorporation of phosphine units were proven by ATR-IR and XRF analytics, additionally the high thermal stability of the network up to 250 °C was shown by TGA measurements. Electronic microscopy and physisorption measurements indicated a permanent micro- and mesoporosity of the amorphous networks (up to 1450 $m^2\ g^{-1}$), which was tailored by the choice of the external crosslinking agents. ^{31}P-MAS-NMR and XPS measurements revealed the electronic structure of the partially oxidized phosphorus species and the cationic character of the metal centers.

In the catalytic experiments, high activities for the hydrogenation of CO_2 to formic acid were achieved, proving the concept of the solid molecular catalyst. The investigations about the structural influence of varying phosphine monomers showed the beneficial properties of bidentate ligands like bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe) or Xantphos for their application as macroligand. Comparative catalytic experiments with homogeneous analogues suggested the retention of the molecular ligand sphere in the immobilized catalysts. Recyclability experiments showed a decrease of the catalytic activity after the first run, resulting in a constant catalytic performance over the following runs. This change can be associated to topological modifications under the catalytic conditions that results in an active and stable catalyst after a certain induction phase.

Acknowledgments
We gratefully acknowledge the Studienstiftung des Deutschen Volkes for the financial support.

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Characterisation and application of the DLP-printed ceramic monoliths for the oxidative coupling of methane process

Marcelina Nowakowska[1*], Anna Rokicińska[2], Piotr Kuśtrowski[2], Piotr Michorczyk[1]

[1]*Department of Organic Chemistry and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland*
[2]*Department of Chemical Technology, Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland*
[*]*marcelina.nowakowska@pk.edu.pl*

Keywords: vat 3D printing, composites, monolithic catalysts, OCM

Introduction. A monolithic catalyst is a block of material with parallel channels that can be, for example, square, round or hexagonal in shape. Through the channels, a stream of liquid or gaseous reactants is transported and the reaction takes way on the inner surface of the hollow channels. Different types of monoliths are used for the processes, including ceramic (e.g. cordierite) or metal (e.g. FeCr alloys) [1-3]. Monoliths are most often obtained by extruding or corrugating the raw material [4], but an innovative method is 3D printing [5]. Monolithic catalysts can be obtained by coating an active layer onto a pure carrier or by adding active components to the finished paste before extruding the monolith [4]. Nowadays, monolithic catalysts are used for the removal of volatile organic compounds (VOCs) and selective catalytic reduction (SCR) of NOx [4,6]. In this presentation, the monolithic catalysts prepared by 3D printing in DLP (digital light processing) technique using composite resins dedicated to oxidative coupling of methane (OCM) have been reported.

Experimental/methodology. Four photo-curable composite (organic – inorganic) resins were prepared for the 3D printer containing 45% alumina and/or kaolin in their composition. Printed ceramic monoliths of the composite resin were burned and then impregnated with solutions containing the active ingredients - 2 wt.% of Mn and 5 wt.% of Na_2WO_4. Next, on each series of monolithic catalysts obtained, the oxidative coupling of methane was carried out at 820°C using a ratio of methane/oxygen of 3.8/1. In addition, X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) were performed for the printed monoliths.

Results and discussion. The application of 3D printing as a technology to obtain monoliths, allowed for the production of precisely defined structures. The development of a method to remove the organic part from the resin made it possible to obtain a pure carrier which, after impregnation with Mn and Na_2WO_4, could be successfully used for oxidative coupling of methane. When the process was performed with a monolithic catalyst and a powder catalyst (the same composition), a comparative yield of C_{2+} hydrocarbons of approximately 18% was obtained in the GHSV value range. However, the great advantage of monolithic catalysts is the lower pressure drop during the reaction than when this occurs with powder catalysts.

Acknowledgments
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The process-structure correlation of VOx/MgO catalysts prepared by solution combustion synthesis for n-octane conversion

P. Ntola[1*], H.B. Friedrich[2], A.S. Mohamed[2], E.J. Olivier[3], A. Govender[4] and S. Singh[2]

[1]Department of Chemistry, Durban University of Technology, Durban, South Africa
[2]School of Chemistry and Physics, University of KwaZulu-Natal, Durban, South Africa
[3]Centre for HRTEM, Physics Department, Nelson Mandela University, Port Elizabeth, South Africa
[4]Group Technology, Sasol South Africa (Pty) Ltd., Sasolburg, South Africa
[*]*pinkies@dut.ac.za*

Keywords: Solution combustion, n-octane, TEM, XRD, fuel effect

Introduction: The conversion of the long-chain linear paraffins into value-added products such as olefins and aromatics is an important industrial process. The oxidative dehydrogenation (ODH) of n-octane may be seen as a viable route to produce the corresponding octenes and C8 aromatics[1]. In ODH of alkanes, the VO_x/MgO system has been reported to form minimum oxygenates and/or cracking products with reasonable selectivity towards ODH products[1]. To attain high activity and selectivity in ODH, it is important to find a catalyst that can activate the C-H bond[2]. This study reports findings of the structural characterization and application of VOx/MgO catalysts prepared by solution combustion synthesis (SCS) using different fuels on the oxidative dehydrogenation of n-octane.

Experimental/methodology: The VO_x/MgO powders were prepared via SCS, using different fuels. The catalysts were then characterized using X-ray diffraction, Raman spectroscopy, SEM and aberration corrected TEM and related techniques. Testing of the catalysts was performed on a continuous flow, fixed-bed reactor operating in vertical flow mode.

Results and discussion: The data demonstrated distinguishable differences in morphology, elemental distribution, phase composition and crystallite size and distribution for the catalyst powders investigated. By correlating experimentally extracted microstructural parameters to calculated thermodynamic parameters we demonstrate the important role of the fuel in controlling the reaction kinetics and in turn the resultant microstructure of the catalyst. Specifically, we highlight the role of a fuel's reducing valency in regulating the maximum temperature and heating rate of a reaction. The best performing catalyst with respect to conversion as well as octene (ODH) selectivity displayed synergistic effects caused by the co-existence of different magnesium vanadate phases (Fig 2). Based on the findings we propose a model of formation for the material system, demonstrating the potential of this novel one-step method for the controlled synthesis of VO_x/MgO powders for catalytic applications.

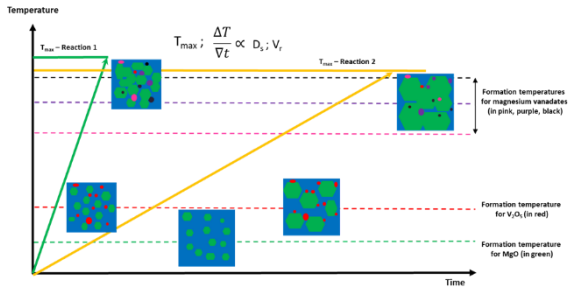

Fig. 1: Graphical representation of a conceptual model for the formation of VOx/MgO catalyats

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CO_2 Hydrogenation Performance of Highly Dispersed Pt and Ru Catalysts Supported on Surface-modified CeO_2 Nanostructures.

A. Molina[1], R. Nuez[1], S. Khannyra[1], D. Goma[1], M.P. Yeste[1], G. Blanco[1], S. Collins[2], D. Motta[3], M.A. Cauqui[1], J.J. Calvino[1*]

[1]*Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Puerto Real (Cádiz), Spain*
[2]*INTEC, CONICET, Santa Fe, Argentina*
[3]*Advanced Photon Source, Argonne National Laboratory, Lemon (Illinois), USA*
[*]*jose.calvino@gm.uca.es*

Keywords: CO_2 methanation, RWGS, ultrathin surface layers, ceria nanoshapes, highly dispersed Pt and Ru

Introduction. Catalytic hydrogenation using green hydrogen sources is currently explored as a route for the valorization of CO_2 into fuels and chemicals. Ceria supported noble metal catalysts stand among systems with potential application in this process, in which both activity and selectivity are influenced by the nature of the metal, their dispersion state and the occurrence of interactions at the metal-ceria interface. Thus, Ru based catalysts seem to favor methanation, whereas those loading Pt directs preferentially the process towards RWGS [1]. In both cases, interaction with Ce^{3+} species and oxygen vacancies play a major role at this respect [2].
Morphology has proven to largely modify the redox response of ceria nanocrystals, as it is also the case of compositional modifications affecting their first few surface layers. Likewise, the activity of noble metals relates intimately to the atomicity of the species (i.e. isolated atoms, subnanometric clusters or metal nanoparticles). Therefore, controlling these variables offer a possible route to modulate both activity and selectivity issues in this reaction.
We have synthesized a series of very low metal loadings (0.1-0.3% wt.) Pt and Ru catalysts highly dispersed onto the surface of ceria nanoxides of different shapes (NanoCubes, NanoRods and NanOctahedra). Furthermore, the redox and acid-base properties of these oxides were modified by mixing Ce with other elements (La, Pr, Zr) at the level of the very first atomic surface layers. Careful characterization of these systems has been undertaken to determine how structure and chemical properties influence performance. Preliminary results point out not only to a large intrinsic activity of the highly dispersed metals but also to a combined contribution of surface crystallography and redox promoters on catalytic performance.

Experimental/methodology. Macroscopic chemical composition was established by ICP-OES and XRF. Macroscopic structural features were determined by XRD. Redox characterization was accomplished using quantitative H_2-TPR experiments and XPS. Metal dispersion was investigated at macroscopic level by EXAFS and FTIR studies of adsorbed CO and, at atomic level, by STEM-HAADF-XEDS.

Results and discussion. As expected, both surface crystallography and the presence of a redox promoter in the first surface layers significantly modify the reducibility of ceria. In all cases, the incorporation of La^{3+} and Pr^{3+} increases Ce^{3+} content in low temperature range (200-500°C). However, such modification affects in a different manner to catalytic performance, which indicates an influence of surface crystallography. Among the different systems, a Ru (0.15% wt.)/ZrO_2 (10%mol)-CeO_2-NC has demonstrated a quite good performance (67% CO_2 conversion, 99% selectivity towards CH_4 at 300°C, H_2:CO_2= 4:1, and 16,000 $cm^3g^{-1}h^{-1}$ GHSV). A large influence of nanoxide morphology is observed in this case. Using a similar feeding, a Pt (0.3% wt)/La_2O_3 (10%mol)-CeO_2-NC catalyst showed almost 50% CO_2 conversion and 96% CO selectivity at 400 °C. Further analysis of these results is currently underway.

Acknowledgments
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Precious-metal-free Catalysts Based on Apatite-type Lanthanum Silicate for Toluene Combustion

N. Nunotani, K. Matsuo, N. Imanaka*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka, Japan
**imanaka@chem.eng.osaka-u.ac.jp*

Keywords: precious-metal-free, toluene combustion, apatite-type

Introduction. Toluene is one of volatile organic compounds (VOCs), which are harmful to human health and the environment. One of effective ways to eliminate toluene is the catalytic combustion. Although Pt-based catalysts have been widely studied due to their high oxidation abilities, such precious-group-metals are expensive and limited resource. Therefore, the development of precious-metal-free catalysts is desired.

Among the precious-metal-free catalysts, $LaCoO_3$ is effective for toluene combustion; however, it requires the elevated temperature of 410°C [1] to oxidize toluene completely. In order to improve the catalytic activity, it is important to introduce promoters which can supply oxygen species toward active sites in $LaCoO_3$. Our previous study demonstrated that apatite-type $La_{10}Si_5CoO_{27-\delta}$ [2] had high oxygen release and storage abilities caused by its one-dimensional tunnel structure suitable for oxide ion conduction and the redox property due to the valence change of $Co^{2+/3+}$ ions. In this study, novel $LaCoO_3/La_{10}Si_5CoO_{27-\delta}/\gamma\text{-}Al_2O_3$ catalysts, composed of $LaCoO_3$ as the activator, $La_{10}Si_5CoO_{27-\delta}$ as the promoter, and $\gamma\text{-}Al_2O_3$ as the support material, were synthesized, and their catalytic activities for toluene combustion were investigated [3].

Experimental. $La_{10}Si_5CoO_{27-\delta}$ was prepared by a sol-gel method. $La_{10}Si_5CoO_{27-\delta}$ was mixed with commercial $\gamma\text{-}Al_2O_3$, and then, $LaCoO_3$ was supported via an impregnation process to obtain 10 wt% $LaCoO_3$/ *x* wt% $La_{10}Si_5CoO_{27-\delta}/\gamma\text{-}Al_2O_3$. Here, the $La_{10}Si_5CoO_{27-\delta}$ loading amount (*x*) was adjusted in the range of 10-30wt%.

Results and discussion. Figure 1 shows the temperature dependence of toluene conversion over the 10 wt% $LaCoO_3$/ x wt% $La_{10}Si_5CoO_{27-\delta}/\gamma\text{-}Al_2O_3$ catalysts. With increasing the $La_{10}Si_5CoO_{27-\delta}$ loading amount (x), the catalytic activity was improved up to *x* = 20, while the specific surface area was decreased (x = 0: 135 $m^2 \cdot g^{-1}$, x = 10: 113 $m^2 \cdot g^{-1}$, x = 20: 87 $m^2 \cdot g^{-1}$, x = 30: 64 $m^2 \cdot g^{-1}$). This improvement might be attributed to the effective oxygen supply from the $La_{10}Si_5CoO_{27-\delta}$ solid. On the other hand, excess introduction of $La_{10}Si_5CoO_{27-\delta}$ decreased the activity, likely due to the low surface area. The highest activity was obtained for the *x* = 20 catalyst among the prepared catalysts, and toluene was completely oxidized at 300°C, lower than $LaCoO_3$ (410°C [1]).

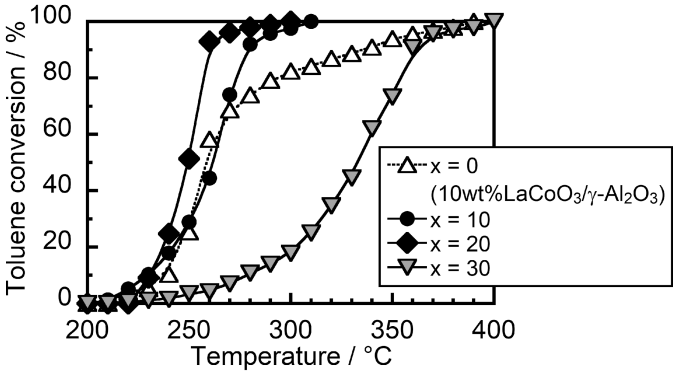

Figure 1. Temperature dependence of toluene conversion over the 10 wt% $LaCoO_3$/ *x* wt% $La_{10}Si_5CoO_{27-\delta}/\gamma\text{-}Al_2O_3$ catalysts.

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Development of new catalytic system driven by vibration energy

Y. Oba, T. Uno, S. Kikkawa, S. Yamazoe*

Tokyo Metropolitan University, Tokyo, Japan
**yamazoe@tmu.ac.jp*

Keywords: Piezoelectric material, Vibration energy, Resonance, Water-splitting

Introduction. Vibrational energy is one of energy sources generated on a daily basis, although the utilization efficiency is not still sufficient. Among the energy from environmental sources, such as solar, geothermal, and vibration, vibration energy can be persistently obtained in natural and man-made structures[1]. The polarization in piezoelectric materials occurs due to the piezoelectric effect when physical stress is applied to piezoelectric devices, resulting in generation of more than 10 V of voltages. In recent years, catalytic reactions using the piezoelectric effect have been reported, such as catalytic reactions using ultrasonic-wave-induced and mechanochemical reactions using ball milling[2,3]. However, the catalytic reaction system driven by low-frequency vibration obtained in our daily life have not been reported. In this study, we demonstrated the low-frequency vibration induced catalytic system using piezoelectric device based on perovskite $Pb(Zr,Ti)O_3$ (PZT), which produces H_2 from H_2O. In addition, a PZT thick-film device was fabricated for the tailor-made design of the "vibro-catalyst".

Experimental/methodology. PZT thick-film devices were fabricated by several methods, such as hydrothermal synthesis, squeegee method, screen printing, and sticking the bulk PZT plate. The vibro-catalytic device consists of a PZT piezoelectric thick film and upper Ag electrode on lower SUS304 plate electrode. Ag electrode was sputtered on the fabricated device. For the evaluation of piezoelectric property and vibro-catalytic activity, one end of the vibro-catalyst was fixed to a holder on a vibrator, and the vessel was vibrated at 150Hz. The vibration was controlled by a waveform generator, amplified by a high-voltage amplifier, and applied them to a vibrator. The H_2 production utilizing a low-frequency vibration was tested by using a flow reactor equipped with a humidifier. The H_2 production activity over a vibro-catalyst was tested under a flow of H_2O-saturated Ar gas at 313 K with applying the vibration at the resonance frequency of 150Hz with connecting SUS to ground. The applied AC voltage between upper and lower electrodes of vibration catalyst (Ag and stainless, respectively) measured by using an oscilloscope was controlled by a high-voltage amplifier and fixed to 13.5 V.

Results and discussion. The XRD patterns of the fabricated PZT devices revealed that the device fabricated by sticking bulk PZT plate showed higher c-axis orientation and morphotropic phase boundaries of tetragonal and rhombohedral structure, which is favorable to high piezoelectric properties. From the time course of catalytic reaction under a vibration applied to the vibro-catalyst at the resonance frequency of 150Hz, H_2 production by H_2O splitting was observed and the formation rate increased with time. The H_2-formation rate reached to 1.0 μmol/h after 24 hours of catalytic reaction. The H_2 production was drastically suppressed when SUS electrode connecting to ground. Thus, we consider that the vibro-catalytic H_2O splitting proceeded by a modulation of electronic state of Ag electrode by the applied AC voltage.

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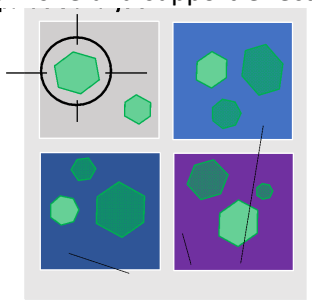
Towards the understanding of structure-function relationships in dry methane reforming using semi-model catalytic systems

J.E. Olszowka[1*], S. Kadam[1], J. Jasik[1], M. Vaidulych[1], K. Simkovicova[1], S. Valtera[1], M. Zlamalova[1], L. Kavan[1], M. Mergl[1], M. Jindra[1], I. Jirka[1], M. Kalbac[1], H. Tarabkova[1], J. Moravkova[1], P. Sazama,[1] Y. Lei[3], A. Kleibert[2], S. Vajda[1]

[1] *J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of Sciences, Prague, Czech Republic*
[2] *Paul Scherrer Institute, Villigen, Switzerland*
[3] *University of Alabama, Huntsville, Alabama, USA*
[*] *joanna.olszowka@jh-inst.cas.cz*

Keywords: Ni nanoparticles, relevant industrial oxides, structure-activity relationship, greenhouse gases

Introduction. In dry methane reforming (DMR), the two greenhouse gases CO_2 and CH_4 are simultaneously converted to the syngas (CO and H_2). Highly active Ni-based catalysts are often used for this reaction, with particle size- and shape dependence determining the catalyst's performance,[1] yet their applications are hampered due to susceptibility to sintering as well as deactivation caused by coke formation. In addition to the exploitation of size effects, the modulation of the metal-surface interactions offers control of the oxidation state, stability and performance of the catalyst over time. In this study, well-defined model catalysts are investigated to identify structure-function relationships derived from size and support effects and to leverage the gained insights for the design of real-world catalysts.



Methodology. Ni NPs are prepared by solvothermal synthesis and deposited on the 2D supporting material with SiO_2, ZrO_2, SnO_2, TiO_2, and Al_2O_3 layers obtained by the ALD on the Si substrate. Materials are characterized *ex-situ* with Scanning and Transition Electron Microscopy, Atomic Force Microscopy, Ellipsometry, and X-Ray Photoelectron Spectroscopy (XPS). Central for the understanding of the factors determining the oxidation state of Ni under working conditions is the characterization by synchrotron-based X-Ray Photoemission Electron Microscopy and XPS with single particle resolution[2] under a flow of CO_2 or CH_4 and their mixture to mimic conditions of DMR.

Selected results. Distinct behavior in the reducibility of Ni NPs is observed when on different supporting materials under DMR conditions. During sequential experiments, a reoxidation of Ni NPs on ZrO_2 is observed by CO_2, followed by subsequent reduction by CH_4. *In-situ* experiments under DMR conditions reveal a reduced Ni and *in-situ* XPS C1s spectra suggest different distributions of the C impurities on the Ni NPs and support material before the reaction, which unifies under high-temperature conditions. SEM images collected on various catalysts after the reaction often reveal a formation of additional carbon deposit over Ni NPs in an encapsulating form of carbon, which might be connected with the porosity of the Ni nanoparticles and the high density of available nucleation sites. Microscopic analysis reveals that in the case of TiO_2 deposited on SiO_2, the thin oxide film can restructure under reaction conditions into islands and depending on the composition of the reactant gas mixture a reduction of TiO_2 to metallic Ti can take place. The presentation will detail correlations between particle size, and the effect of the support and oxidation state of Ni as main parameters for balancing and optimizing performance and stability.

Acknowledgments

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Ge outperforms other zeolite sites in sucrose-to-HMF conversion

M. Opanasenko*, P. Rani, M. Shamzhy

Charles University, Prague, Czech Republic
**maksym.opanasenko@natur.cuni.cz*

Introduction. In a view of utilization of catalysis for emerging applications, enormous efforts are being made to transform renewable biomass (cellulose, carbohydrates, etc.) into fuels and value-added chemicals. Among biomass-derived platform chemicals, 5-hydroxymethylfurfural (HMF) is regarded as versatile building block which can be further transformed into valuable derivatives (furandicarboxylic acid, dimethylfuran, bis(hydroxymethyl)furan, etc.) used as precursors in the polymer industry and liquid fuels. The synthesis of HMF from sucrose is a multistep process. All steps are facilitated by the acid sites. Classical zeolites (aluminosilicates), as well as 4-valent element (Sn, Zr) substituted zeolites, have high acidity and therefore exhibit high activity for biomass transformation. In particular, 10-ring and 12-ring zeolite catalysts found to be promising candidates in most studies [2, 3].

Experimental/methodology. Different types of zeolites, such as extra-large UTL and CTH and large-pore IWW were prepared. The most sustainable germanosilicate (Ge-IWW) was modified with the different heteroatoms such as Sn, Zr, and Al (the elements shown to be the most promising for HMF synthesis up to now) for a comparative study. The idea of the work consisted in the design of materials with fixed structure and variable nature of active sites (and vice versa). Although the selected solids are costly and complex in preparation, they allow to incorporate all desired elements and thus they can be used as model systems to understand the influence of the mentioned aspects on the catalytic activity of zeolites in HMF synthesis.

Results and discussion. Catalytic investigation showed that Ge-IWW zeolite exhibits the optimum activity and stability compared to Ge-UTL and Ge-CTH. Heteroatom substitution in the IWW framework allowed to relate the output of sucrose to HMF transformation with the nature of acid sites in catalysts. Zr-IWW zeolite exhibited moderate product selectivity; however, the HMF yields obtained over heteroatom-substituted IWW zeolites are lower than those obtained on the Ge-IWW zeolite confirming that the presence of Ge atoms in the zeolite framework enhances the efficiency of the catalyst for this particular reaction. The presence of labile Ge-O-Si bond enhances the possibility for creation of Brønsted acid sites which are required for hydrolysis of sucrose to hexose. This study demonstrates that germanosilicates are worth considering for synthesis of value-added chemicals via biomass-based catalysis.

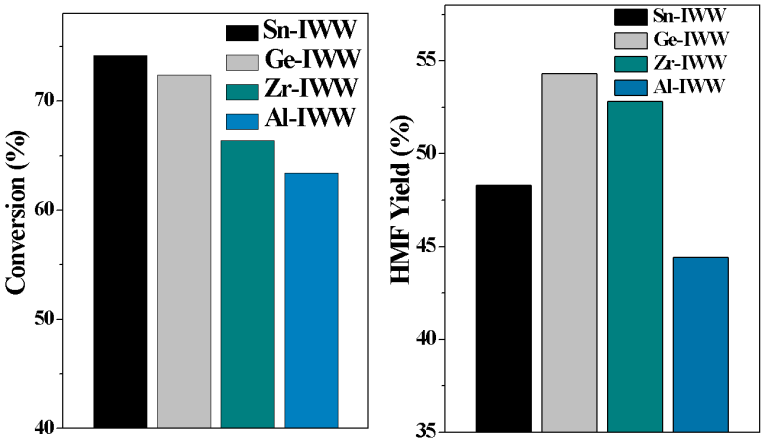

Figure 1. Sucrose conversion (a) and HMF yield (b) over zeolites with the same structure but different active sites.

Acknowledgments
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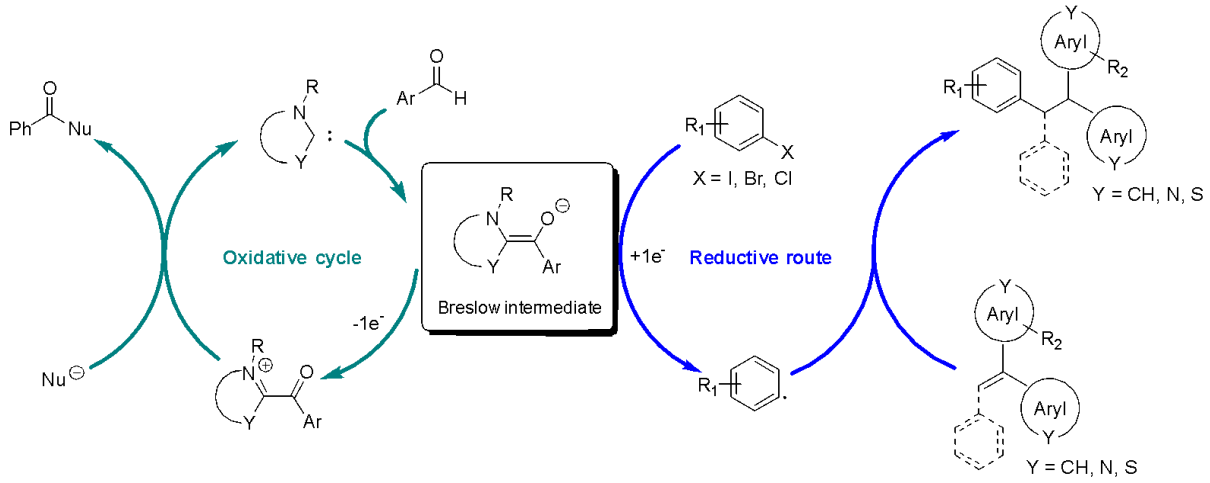
Concomitant oxidative and reductive transformations from *N*-Heterocyclic carbene organocatalysis

Nadhrata ASSANI,[1] Ludivine DELFAU,[2] Eder TOMAS-MENDIVIL,[2] Sébastien REDON,[1] Patrice VANELLE,[1] David MARTIN,[2] Julie BROGGI[1*]

[1]*Aix Marseille Université, ICR, UMR 7273, Faculté de Pharmacie, 13005 Marseille, France. (e-mail: julie.broggi@univ-amu.fr)*
[2]*Département de Chimie Moléculaire, UMR CNRS 5250, CS 40700, 38000 Grenoble, France. (e-mail: david.martin@univ-grenoble-alpes.fr)*

The last decade, a multitude of organocatalyzed transformations of carbonyl derivatives took advantage of the oxidation of Breslow intermediates, arising from the reaction of these carbonyl substrates with stable N-Heterocyclic Carbenes (NHCs). However, valorization of the electrons lost during these oxidative transformations had not been addressed until recently. In 2021, Ohmiya and Bertrand independently demonstrated that these Breslow intermediates can also be used as formal reductants.[1][2] NHC-organocatalyzed arylacylations of diverse alkenes were thus performed upon reduction of iodoaryl derivatives into radical species. In their reaction, the aldehyde used to generate the Breslow enaminol was also integrated in the final addition product.

In this new study, our objective was to develop a strategy where the Breslow enolate catalyst both serves as an electron source for challenging reductive transformations and as key intermediate for the valorization of aldehydes through oxidative transformations. Our strategy thus allowed the interdependent formation of two distinct products through concomitant oxidative and reductive transformations. We also focused on novel sources of NHCs and aldehydes to generate more powerful Organic Electron Donors (OEDs).[3][4] Imidazolylidene-based enaminols proved to be powerful donors for the single-electron transfer reduction of various challenging substrates. The generated radical intermediates were further exploited in arylations of alkenes while the sacrificial aldehydes were valorized through oxidation reactions.



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Heterogenization of Iron Schiff Base Complex for Catalysis

Tianyu Gao[1], Zhen Yan[2], Martine Trentesaux[1], Maya Marinova[3], Vitaly Ordomsky[1], Sébastien Paul

[1]Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France
[2]E2P2L, UMI 3464 CNRS-Solvay, 3966 Jin Du Rd., 201108 Shanghai, China
[3]University of Lille, CNRS, INRAE, Centrale Lille, University of Artois, FR 2638 IMEC Institut Michel-Eugène Chevreul, F-59000 Lille, France

[*]Corresponding Author's E-mail address: sebastien.paul@centralelille.fr

Keywords: catalysis, COF, heterogenization, Schiff chemistry, iron.

Introduction. Transition metal Schiff base complexes are known to act as efficient homogeneous catalysts for organic reactions such as oxidation, alkylation, isomerization, etc. However, they often suffer from low stability and are difficult to separate from the reaction medium after use.

Experimental/methodology. In this work, we propose a method of heterogenization of this kind of catalysts using a Covalent Organic Framework material (COF) synthesized by Schiff chemistry, which can incorporate metal ions such as Fe^{3+}. A slightly modified procedure for the synthesis of LZU1 COF was proposed by using hydroxyl substituted 2,5-diaminohydroquinone with 1,3,5-triformylbenzene.

Results and discussion. It resulted in the generation of sites containing two hydroxyl groups and imine groups able to coordinate with Fe(III) cations like in a conventional Schiff complex (Figure 1). The prepared material possesses a two-dimensional eclipsed layered-sheet structure with uniform distribution of Fe and demonstrated a high catalytic activity, comparable to those of the homogeneous Fe catalyst, together with high stability and recyclability in the model reaction of epoxidation of styrene to styrene oxide by H_2O_2.

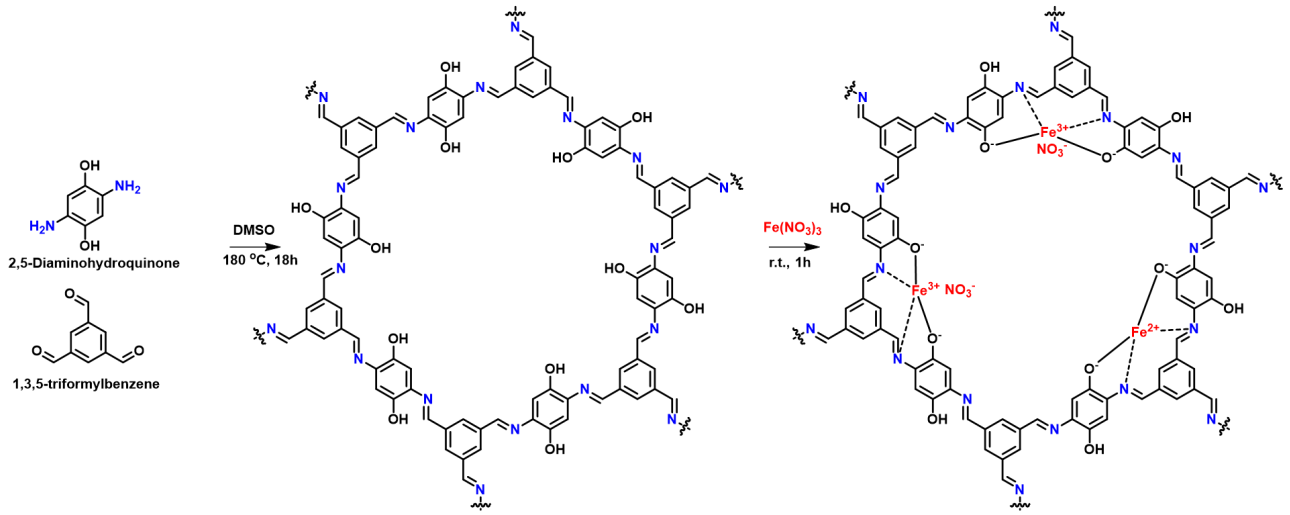

Figure 1. Scheme of the synthesis of COF and Fe-COF

Acknowledgments

The authors thank Solvay for the financial support. The Chevreul Institute is thanked for its help in the development of this work through the ARCHI-CM project supported by the "Ministère de l'Enseignement Supérieur de la Recherche et de l'Innovation", the region "Hauts-de-France", the ERDF program of the European Union and the "Métropole Européenne de Lille". The authors would like to thank Florent Blanchard and Ahmed Addad for their help in carrying out the work on the X-Ray diffraction and electron microscopy facilities of the Advanced Characterization Platform of the Chevreul Institute. The authors also thank Olivier Gardoll and Joelle Thuriot for their help in TGA and XRF measurements. Tianyu Gao thanks the China Scholarship Council (CSC N°: 201807030012) for the financial support of his PhD.

Novel aerosol-made CuO-CeO_2 catalysts with superior CO oxidation activity

G. Pampararo[1], E. Sartoretti[2], S. Bensaid[2], D. P. Debecker[1*]

[1]*Université catholique de Louvain (UCLouvain), Institute of Condensed Matter and Nanosciences (IMCN), Place Louis Pasteur, 1, 1348 Louvain-la-Neuve, Belgium*

[2]*Politecnico di Torino, Dipartimento Scienza Applicata e Tecnologia (DISAT), Via Enrico d'Ovidio 10, 10129, Torino, Italy*

[*]*damien.debecker@uclouvain.be*

Keywords: Copper-Ceria catalysts**,** aerosol processing, mesoporous materials, CO oxidation

Introduction. Among the alternatives to the noble metal based systems for the abatement of carbon monoxide, Cu is often chosen to enhance the ceria reactivity, and the system has proven to be promising [1,2]. Moreover, beneficial effects on catalytic performance have been evidenced when favoring (i) a stronger interaction between CuO and CeO_2, (ii) higher specific surface area, (iii) small pores with a homogeneous distribution [3]. Nevertheless, in this system, most catalysts reported in literature are synthesized by methods that neither allow to precisely control textural and morphological properties nor favor an intimate mixing between the two phases. Exploring innovative catalysts syntheses is arguably the keystone to round these corners and to reach higher catalytic performance. Along this line, the aerosol-assisted sol-gel process (AASG), which is emerging as a powerful route to produce various nanomaterials and in particular tailored heterogeneous catalysts [4,5] is primed to solve the above-mentioned challenges.

Experimental/methodology. Here we report, for the first time, aerosol assisted sol gel made CuO-CeO_2 catalysts (denoted as A-CuxCe, where "x" is the Cu wt. loading) employed for the Low Temperature CO Oxidation (LTCO). AASG catalysts have been synhtesized by atomization of the precursors solution (cerium and copper nitrates witha templating agent, in an ethanol/water solution), followed by rapid processing (reactive drying) in a tubular furnace. Templating agent removal and porosity formation has been carried out by a controlled calcination step under static air, up to 723 K. Aerosol made materials are then compared with a series of benchmark catalysts made by impregnation (denoted as I-CuxCe). Catalysts were tested for CO oxidation using a temperature ramp or sets of isothermal steps, with an online IR monitoring of reactants/products concentrations. Performance is interpreted in the light of in-depth characterization surveys (XRD, in situ XRD, N_2 physisorption, DRIFT, TPD, XPS, Raman, (S)TEM).

Results and discussion. Considering pristine CeO_2, X-ray diffraction patterns show that the commercial CeO_2 is composed of 40 nm-sized crystallites, while A-CeO_2 features much smaller crystallites (8 nm). The aerosol-made CeO_2 had a specific surface area (SSA) as high as 130 m²/g, with a narrow pores distribution centred around 5-6 nm while the commercial ceria shows only a SSA of 5 m^2/g and a bigger pore distribution centred at 25 nm. For A-CuxCe catalysts, up to 10% wt of Copper, characteristics peaks of CuO are not detected, revealing very small dimensions compared to the impregnated one with the same loading, i.e. CuO cristallites of 35 nm.Upon introduction of Cu, the textural properties remained similar (115 m^2/g for A-Cu10Ce versus 3 m^2/g for I-Cu10Ce). Thus, is clear that the fast atomization and polycondensation of the precursors allows to produce materials with a higher surface area and porosity, with smaller cristallites and much more dispersed active species. Looking at the catalytic activity, aerosol-made catalysts are impressive. For example, A-Cu10Ce (only 10% Cu) shows already ~20% conversion at 323 K and reaching complete CO conversion at 360 K. This temperature is at least 30 K lower than the state-of-the-art catalysts [6].

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Promotion of Palladium Nanoparticles by Amine-Modified Ionic Liquid Polymers Towards CO_2 Hydrogenation to Formate

R. Paterson[1*], T. W. Chamberlain[2], E. Arca[1], J. G. Knight[1], S. Doherty[1]

[1]*School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, UK*
[2]*School of Chemistry, Leeds University, Leeds, UK*
[*]*r.paterson@newcastle.ac.uk*

Keywords: Ionic liquid, carbon dioxide hydrogenation, nanoparticle, formate

While the coordination of ligands to homogenous metal complexes is well-defined, the interaction between heterogenous metal clusters and functionalized supports is still not understood. Polymer immobilized ionic liquids (PIILs) have been shown to be effective supports for the stabilization of metal nanoparticles for use as catalysts in a range of transformations.[1] The modular synthesis of PIILs allows for the control of the support ionic microenvironment and for the employment of surface functionality, thereby influencing nanoparticle size/morphology as well as their efficacy and stability as catalysts. Moreover, there is mounting evidence that the surface electronic structure of a catalyst can be manipulated by the incorporation of a heteroatom donor which has been shown to enhance efficacy.[2] Recently, we reported that platinum nanoparticles stabilized by a phosphine-modified PIIL catalyze the hydrolytic release of hydrogen from sodium borohydride,[3] while phosphine oxide functionalized PIIL supported ruthenium nanoparticles catalyzed the selective reduction of nitrobenzene to *N*-phenylhydroxylamine under mild conditions.[4]

In this work, amine-modified PIIL supports were used to stabilize *in-situ* generated palladium nanoparticles (PdNP) for the thermal hydrogenation of CO_2 to formate in the presence of base. PdNP stabilized by an arylamine functionalized PIIL outperformed its benzylamine counterpart, and both catalysts were found to be superiour to unmodified PIIL-supported PdNP (**Figure 1**). Further, catalyst performance was shown to improve with increasing loading of the amine on the polymer support. Influence of the amine on catalyst efficacy is now being explored with XPS and HRTEM.

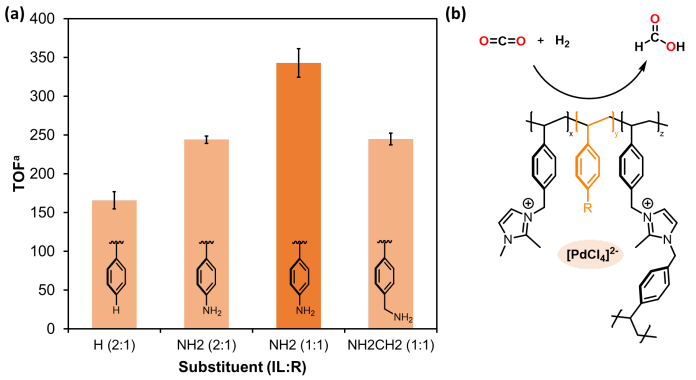

Figure 1: (a) Plot of turnover frequency against catalyst support, where polymer composition IL:R = (x+z):y . **(b)** Schematic of CO_2 hydrogenation to formic acid by catalyst precursor $PdCl_4$@PIIL, where substituents R are described in (a). [a] $mol_{formate}/mol_{Pd}/hour$

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Co-Ru/SiC as catalyst for ammonia decomposition reaction

M. Pinzon[1], A. Romero[2], A. de Lucas-Consuegra[1], A.R. de la Osa[1], P. Sánchez[1]
[1]*Department of Chemical Engineering, Faculty of Chemical Sciences and Technologies,* [2]*Higher Technical School of Agronomical Engineers, University of Castilla-La Mancha, Ciudad Real, Spain*
[*]*marina.pgarcia@uclm.es*

Keywords: Hydrogen, ammonia decomposition, bimetallic catalysts

Introduction. Decomposition of ammonia (NH_3) is an efficient technology for generating CO_x-free hydrogen (H_2). The design of an active catalyst to optimize the reaction conditions is one of the main challenges of this technology. In this sense, both the active phase as well as the support, have an important role in the catalytic activity [1]. Carbide species have shown excellent results as support of different catalytic metals. Previous studies of our research group indicated that ruthenium and cobalt supported on silicon carbide (SiC) exhibited suitable ammonia conversion at low temperatures [2]. However, bimetallic catalysts have not yet been studied over SiC. Therefore, the target of this work was to develop for the first time Ru-Co bimetallic catalyst supported on structured SiC for the H_2 production from NH_3. The influence of the order of incorporation of the metals into the support and the Ru/Co ratio were optimized.

Experimental/methodology. Firstly, three different sets of catalysts were prepared in a different way, with a total metal loading of 5 wt% and Ru/Co weight ratio equal to 50/50. They were called Co/Ru/SiC and Ru/Co/SiC, which refers to the metal impregnation order with an intermediate calcination step (500 °C, 1 h), and Co-Ru/SiC which refers to the catalyst prepared by co-impregnation. Finally, all catalysts were calcined at 500 °C, 1 h (under N_2). The influence of the Ru/Co ratio (50/50 and 20/80) was studied using the catalysts prepared by co-impregnation with a total metal loading of 2.5 wt%.

Results and discussion. Table 1 shows the metal content (from EDS analysis), the mean particle size evaluated by TEM images, and the catalytic activity at 350 °C of prepared catalysts. For comparative purposes monometallic samples has been included. It was shown that the metal order impregnation affected the particle diameter, and hence, the catalytic activity, due to the structure-sensitive character of the reaction [2]. The lower metal particle size and the suitable metal content of the catalyst prepared by co-impregnation method could explain the superior catalytic activity showed by Co-Ru/SiC catalyst being only a 30% lower than Ru/SiC even when Ru content was halved. On the other hand, the study of metal loading (not shown here) concluded that it is possible reduce the metal content until 2.5 wt% by keeping an excellent activity [2]. Finally, the Ru/Co ratio (Table 1) indicates that the Ru presence was essential to achieve high conversion, exhibiting the 50Co-50Ru/SiC better catalytic activity than pure cobalt catalysts. Ru has been established to be highly active for this reaction [1] but it is limited and expensive. However, this work has allowed to synthesize a novel bimetallic catalyst with low metal loading of this critical noble metal.

Table 1. Metal content, particle size and NH_3 conversion at 350 °C (5v/v%NH_3-Ar, GHSV=60000 mL·g^{-1}·h^{-1}, 1 atm)

	Order impregnation (5 wt%)					Ru/Co wt. ratio (2.5 wt%)		
Samples	**Co/Ru/SiC**	**Ru/Co/SiC**	**Co-Ru/SiC**	**Co/SiC**	**Ru/SiC**	**50Co-50Ru/SiC**	**80Co-20Ru/SiC**	**Co/SiC**
Metal content (wt %) Co/Ru	2.4/2.0	0.46/3.1	2.4/3.6	-	-	1.4/1.9	3.1/0.6	-
TEM-Particle size (nm)[a]	8.8	7.8	7.1	10.3	7	-	-	-
NH_3 conversion (%)[a]	39.8	61.2	63.1	34.4	90.1	43.9	31.9	21.2

[a]From the reduced catalysts at 400 °C (50% H_2/Ar).

Acknowledgments
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Enhancing the activity of IrO_x catalysts for OER in PEM electrolysers

S.Pitscheider[1*], C.M.Pedersen[1], E. Bertheussen[1], S.R.Cooper[1], A.Maletzko[2], E.D.Gomez Villa[2], J.Melke[2], N.Seselj[3], A. Bornet[4], G. Wiberg[4], M. Arenz[4], C.Kallesøe[1]

[1]*Danish Technological Institute, Taastrup, Denmark*
[2]*Fraunhofer Institut für Chemische Technologie, Pfinztal (Germany)*
[3]*Blue World Technologies, Kvistgård, Denmark*
[4]*University of Bern, Bern, Switzerland*
[*]*sip@teknologisk.dk*

Keywords: PEM electrolysis, low-CRM, catalysts

Introduction. Proton exchange membrane water electrolysers (PEMWE) are widely regarded as the most active and flexible of all electrolyser technologies. However, the catalyst materials needed for the oxygen evolution reaction (OER) in PEM conditions are one of the main limiting factors towards a widespread market uptake of the technology, due to their scarcity, price and challenges with long-term stability. [1] Reducing the amount of critical raw materials (CRM) in the anodes of PEMWEs, is crucial to bring the technology to the scale needed to efficiently store renewable electricity as green hydrogen.

Experimental/methodology. Supported Ir and IrRu nanoparticles were synthesized on Sb-doped SnO_2 (ATO) in a supercritical flow synthesis, which allows for a fine tuning of the nanoparticles size and oxidation state. [2] The catalyst materials were hereafter characterised using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) to assess their elemental composition, X-ray diffraction (XRD) and pair distribution function (PDF) analysis to assess their crystalline properties, transmission electrode microscopy (TEM) to visualize their microstructure, and rotating disk electrode (RDE), gas diffusion electrode (GDE) and single cell measurements to assess their electrochemical activity.

Results and discussion. The supported Ir nanoparticles exhibited a considerable boost in activity in comparison to unsupported Ir (Figure 1), which was further enhanced by adding Ru in the catalyst. Moreover, the presence of Ni during the synthesis promoted the creation of a more active phase with a more amorphous character. [3] This allowed obtaining high performance with lower catalyst loadings in single cell measurements, albeit with stability issues that will need to be resolved with microstructural optimisation.

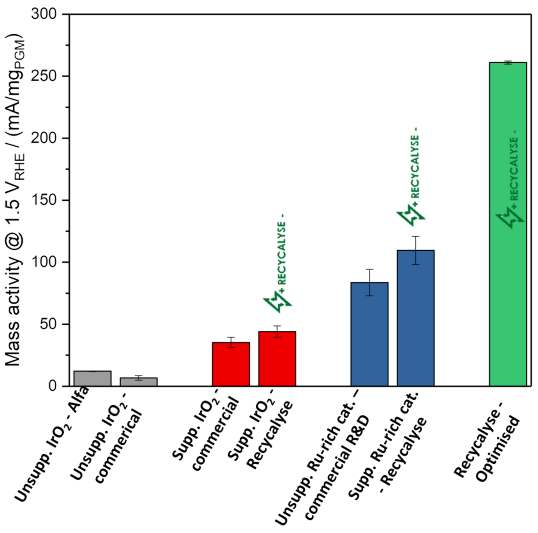

Figure SEQ Figure * ARABIC 1: Comparison of the electrochemical activity of unsupported IrO_2 and improved supported catalysts.

Acknowledgments

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Vanadium: an efficient promoter for Ni based catalyst for Methane Dry reforming

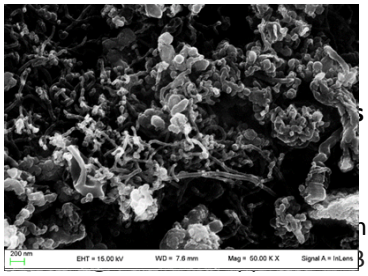
M. Pizzolato[1*], G. Da Pian[1], A. Di Michele[2], G. Cruciani[3], F. Menegazzo[1], M. Signoretto[1]

[1]*Ca' Foscari University, Venezia, Italy*
[2]*University of Perugia, Perugia, Italy*
[3]*University of Ferrara, Ferrara, Italy*
[*]*marco.pizzolato@unive.it*

Introduction. Hydrogen is an advantageous energy vector. A new sustainable approach for synthesizing hydrogen could be Methane Dry Reforming (MDR). However, applying this reaction at an industrial level could be impeded by its high endothermicity, and the difficulty to formulate a robust catalyst. Among the metals Ni has attracted the most attention due to its good activity for MDR. However, it can also catalyze side reactions such as Bouduard or Methane Cracking leading to coke formation. Vanadium element was selected as promoter because it can improve the dispersion of nickel, enhancing the activity and preventing the sintering process [1]. Furthermore, the ability to adsorb CO_2 can be improved, forming monodentate carbonates, that are the intermediates responsible of CO_2 activation [2]. As co-promoter calcium was selected because it should limit carbon coke formation. All these characteristics can be suitable for this work purposes. In this study, three samples were compared: bare Ni/Al_2O_3 as reference, $Ni\text{-}V/Al_2O_3$, and $Ni\text{-}V\text{-}Ca/Al_2O_3$ to evaluate whether the introduction of these additional doping agents can further improve the activity and the stability of the catalyst.

Experimental/methodology. The catalysts were prepared by incipient wetness impregnation to obtain 10 wt. % of Ni, 1 wt.% of V and 10 wt.% of Ca in the final material. Catalysts were also characterized using different techniques such as ICP-OES, N_2 physisorption, TPR, XRD, DRUV-Vis, SEM-EDX, and TPO. The catalytic tests were carried out at 650 °C in a fixed bed reactor with a GHSV of 12000 h^{-1} and a reagent ratio (CH_4:CO_2:He) of 1:1:18.

Results and discussion. The introduction of vanadium in Ni based MDR catalysts was effective, and a homogeneous metal dispersion was obtained, as confirmed by EDX analyses. Activity tests confirmed that vanadium enhanced the activity and stability of catalyst over 100 h reaction compared to the non-doped catalyst, which suffered from a faster deactivation. In fact, for the promoted sample containing vanadium, also a boost of hydrogen yield was obtained in diluted conditions test. Furthermore, from spent catalysts characterizations, a lower deposition of nanotubes was detected on promoted $Ni\text{-}V/Al_2O_3$ catalyst. With the introduction of Ca, this phenomenon was further enhanced as it could be seen in SEM-EDX images. In addition, in stress tests vanadium led to a higher conversion of reagents with a 30% increase for CH_4, and 15% increase for CO_2. It can be concluded that vanadium is a valuable promoter for Ni/Al_2O_3 catalysts for Methane Dry Reforming.



b) c)

s deposits on spent (a) Ni/Al_2O_3, (b) $Ni\text{-}V/Al_2O_3$, and (c) $Ni\text{-}V\text{-}Ca/Al_2O_3$ after 100h on

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MgO-Induced Structure Sensitivity in Cu-Based Catalysts Synthesized via a Novel Precursor Route for CO_2 to Methanol Conversion

Meenakshi Pokhriyal[1], *Aakash Bhardwaj*[1], *Sreedevi Upadhyayula*[1]*

[1]*Department of Chemical Engineering, Indian Institute of Technology, Delhi, India*

* *sreedevi@chemical.iitd.ac.in*

Introduction. Methanol today is not only the most important feedstock for chemicals and fuel components but also is an important chemical and a potential energy carrier in the future. Since the early 1960s hitherto, $Cu/ZnO/Al_2O_3$ ternary catalysts developed by Imperical Chemical Industries have been used commercially for methanol synthesis derived from the malachite rosasite synthesized precursors [1]. In recent years Mg^{2+} which is an interesting replacement for Zn^{2+}, not only because of the close match in the ionic radii, charge but also of the similarity in precursor formation chemistry with Cu^{2+}. Moreover, it promotes the number of CO_2 and H_2 adsorption active sites and increased the metal-support interaction with high metallic Cu surface area [2]. These catalysts have been found to be structure sensitive and the activity varies depending on the conditions employed in the very first stage of catalyst synthesis i.e., precursor formation [3]. However, conventional methods of precursor synthesis suffer from interference of competing phases which ultimately lead to the activity deterioration in the final catalyst. To overcome these difficulties in the present case Cu/MgO catalyst has been synthesized using an optimized hydrothermal based precursor formation approach for the first time with an improved and efficient outcome for hydrogenation of CO_2 to methanol. The precursor and final catalyst have been characterized with an array of instrumental techniques.

Experimental. For the synthesis and optimizations of Cu-MgO catalyst, firstly the synthesis of hydroxy carbonate precursor has been carried out using a hydrothermal route using nitrate salts as reactant in the presence of carbonating agent at different set of temperature and varied durations. The pure catalyst formed were then calcined at 350 °C and 400 °C for 3 h in static air individually. The catalytic activity tests were performed in a fixed-bed reactor connected with gas chromatography for product analysis.

Results and discussion. The PXRD pattern of the product obtained is shown in Figure 1. The pattern showed a complete resemblance with the Mcguinnessite which is a Rosasite like structure. The precursor as well as catalyst obtained after calcination showed low crystallite size, high surface area with a unique spongy ball like shape unlike already reported catalysts. The catalytic activity optimizations and results using CM-HT showed that the best optimized operating condition was T= 240 °C and P= 40 bar, at which the highest catalytic performance was achieved. The CO_2 conversion of 21.78%, methanol selectivity of 73.43%, and methanol yield of 8.62 $mg_{methanol}.gcat^{-1}.hr^{-1}$ were calculated in terms of space-time yield.

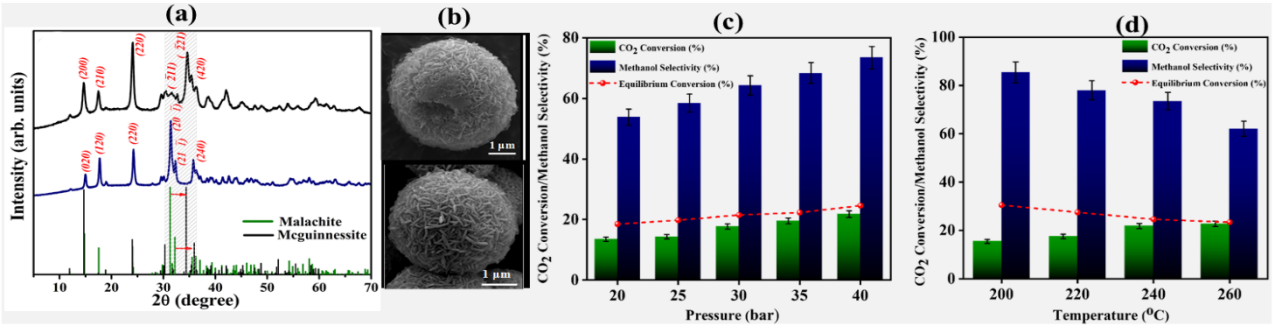

Figure 1: (a) PXRD pattern of Cu-Mg hydroxy carbonate precursor synthesized via hydrothermal route, (b) FESEM images of precursor and calcined catalyst, (c) Effect of pressure at 240 °C and (d) Effect of Temperature at 40 bar pressure and 2600 WHSV on the catalytic performance.

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Preparation of supported bimetallic RuCo catalysts

Ž. Ponikvar[1*], A. Sedminek[1], J. Teržan[2], B. Likozar[2], D. Makovec[1], S. Gyergyek[1]

[1]*Jozef Stefan Institute, Ljubljana, Slovenia*
[2]*National Institute of Chemistry, Ljubljana, Slovenia*
[*]*ziga.ponikvar@ijs.si*

Keywords: bimetallic, alloy, supported, composite, catalyst

Introduction. Noble metal catalysts have proven to be effective for numerous applications, one of the most researched topics currently being ammonia decomposition. Ammonia can be safely transported and decomposed to produce hydrogen on-demand. Among noble metals, Ru boasts the best catalytic performance, however, it is scarce and costly. Alloying it with abundant metals could help lower the required Ru content due to increased activity [1].

Experimental/methodology. The catalysts were prepared by adsorption of RuCo precursor nanoparticles onto a high-surface area alumina support followed by reduction of the precursor to metallic RuCo. In the first step, the support was prepared. AlN was hydrolyzed in an aqueous suspension of silica nanoparticles (30 wt.%) which serve as nucleation seeds for boehmite. The boehmite was dehydrated to form *γ*-alumina by heat treatment at 500 °C in stagnant air. RuCo precursor nanoparticles were prepared by co-precipitation of Ru^{3+} and Co^{2+} achieved by a drop-wise addition of 2 M NaOH during vigorous stirring until achieving a pH level of 10. The precursor nanoparticles were mixed with the support for 10 min to give the particles ample time to adsorb. The material was freeze-dried and reduced in a tubular furnace at 500 °C in hydrogen (150 mL/min). The catalysts were characterized using Transmission electron microscopy (TEM) and Vibrating sample magnetometry (VSM). Catalytic activity was determined using a fixed-bed reactor.

Results and discussion. Co-precipitation of Ru^{3+} and Co^{2+} results in a formation of nanosized particles where both cations are relatively homogenously mixed. When alumina support is added, precursor nanoparticles adsorb onto its surface. Reduction at 500 °C in a hydrogen atmosphere leads to a complete conversion of precursors to alloyed RuCo nanoparticles. Detailed elemental analysis using Energy dispersive X-ray spectroscopy (EDXS) in TEM showed that composition of individual RuCo nanoparticles is close to the nominal composition of 10 wt.% of Ru and 90 wt.% of Co. The size of individual RuCo nanoparticles ranges from 10–20 nm (Figure 1 a and b) while their distribution over the support's surface is not exceptionally homogenous (Figure 1 a). Measurements of room temperature magnetization curves reveal soft ferromagnetic behavior, a saturation magnetization of 25 emu/g and coercivity of 635 Oe. Over the course of one month, the saturation magnetization drops to a value of 16 emu/g indicating surface oxidation. Observation of individual RuCo nanoparticles using TEM indicates a formation of a thin oxide shell (Figure 1 b). Further studies were devoted to improving homogeneity of RuCo nanoparticle distribution, detailed investigation of their oxidation behavior and the influence on magnetic and catalytic properties.

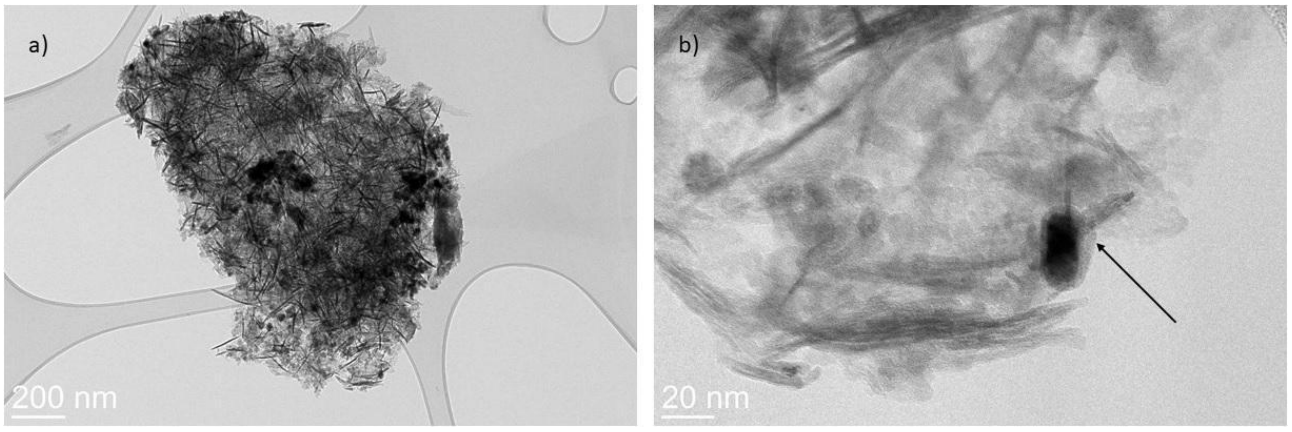

Figure 1: A RuCo/alumina composite catalyst particle (a) and an embedded RuCo particle with the surrounding oxide shell marked with an arrow (b) observed using TEM.

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Speeding up synthesis of nanolayered zeolites synthesis by interzeolite transformation

Peerapol Pornsetmetakul,[1,2] Chularat Wattanakit,[2*] Emiel J.M. Hensen[1*]

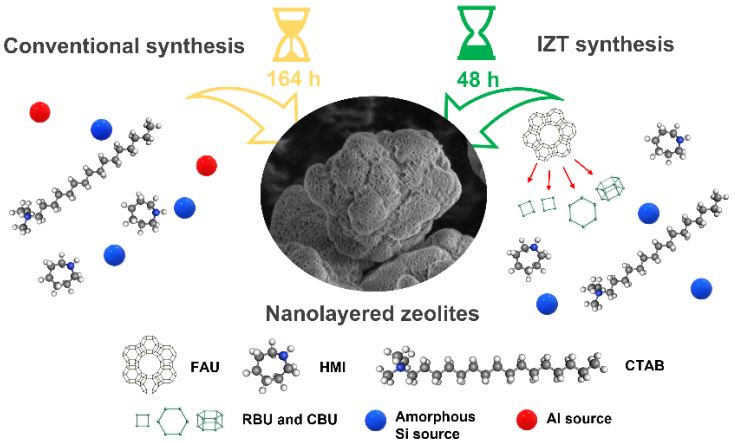
[1] *Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands.*
[2] *School of Energy Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong, 21210, Thailand.*
*chularat.w@vistec.ac.th , *e.j.m.hensen@tue.nl*

Keywords: Zeolite synthesis, Interzeolite transformation, Nanolayered catalyst

Introduction. Hierarchically nanostructured zeolites exhibit many benefits over conventional bulk zeolites in the conversion of petroleum-based and bio-based feedstocks to chemicals.[1, 2] However, the synthesis of such zeolites is typically time-consuming and requires complex organic templates or various steps to achieve well-defined and interconnected micro- and mesopores. Therefore, a fast and facile yet economically efficient synthesis of such zeolites would be very welcome.

Experimental/methodology. Herein, the one-pot synthesis of nanolayered MWW and FER zeolites was accelerated by the interzeolite transformation (IZT) approach. FAU (faujasite zeolite) was used as the Al source and partial Si source, while HMI (hexamethyleneimine) and CTAB (cetyltrimethylammonium bromide) served as micropore directing and intercalating agents, respectively. A combination of XRD, SEM, Ar physisorption, ^{29}Si and ^{27}Al NMR, and Raman spectroscopy were used to track morphological and structural changes as a function of crystallization time of these two approaches.

Results and discussion. Compared with conventional MWW synthesis at a similar gel SiO_2/Al_2O_3 ratio of 25, the IZT approach offers a reduction of the synthesis time from 164 h to 48 h and provided crystalline MWW with a similar nanolayered morphology (Figure 1). Adjustment of the SiO_2/Al_2O_3 to 15 for the IZT synthesis gel affords nanolayered FER. Characterization indicates that IZT accelerated the formation of MWW topology via transfer of sharing 4MR units from the FAU source to MWW, while CTAB intercalates between the layers, thereby directing the nanolayered morphology. These phenomena are similar to those observed



in conventionally microporous zeolite synthesis via IZT[3, 4] and conventional synthesis of nanolayered MWW.[1] The benefit of nanolayered zeolites follows from the strongly improved performance in Diels-Alder cycloaddition reactions useful for obtaining biobased p-xylene. Facile zeolite synthesis via IZT is versatile with respect to zeolite topology.

Figure 1 Scheme of nanolayered zeolite synthesis accelerated by IZT compared with conventional synthesis.

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Thermal synthesis of graphitic carbon nitride in argon atmosphere for photocatalytic hydrogen evolution

Petr Praus[1,2], Lenka Řeháčková[1], Jakub Čížek[3], Aneta Smýkalová[1,2], Martin Koštejn[4], Jiří Pavlovský[1], Miroslava Filip Edelmannová[2], Kamila Kočí[2]

[1]Department of Chemistry and Physico-Chemical Processes, VŠB-Technical University of Ostrava, 17. listopadu 15, 708 00 Ostrava-Poruba, Czech Republic
[2]Institute of Environmental Technology, CEET, VŠB-Technical University of Ostrava, 17. listopadu 15, 708 00 Ostrava-Poruba, Czech Republic
[3]Department of Low-Temperature Physics, Faculty of Mathematics and Physics, Charles University, V Holesovickach 2, Prague 8, Czech Republic
[4]Institute of Chemical Process Fundamentals, Czech Academy of Science, Rozvojová 1, 165 02 Prague, Czech Republic

Keywords: graphitic carbon nitride, thermal synthesis, argon atmosphere, nitrogen vacancies, photocatalytic hydrogen evolution.

Abstract. Graphitic carbon nitride (g-C_3N_4) is a two-dimensional and metal free polymeric material with semiconducting properties that has been intensively studied during the last decade. Among its noteworthy properties are high thermal, physical, chemical, and photochemical stability. G-C_3N_4 absorbs visible light as a result of the band gap energy of ca. 2.7 eV. It can be prepared by physical or chemical vapour deposition but bulk synthesis from simple precursors by methods focused on the thermal condensation of nitrogen-rich precursors, such as cyanamide, dicyandiamide, melamine and so forth, are mostly used. Graphitic carbon nitride has been synthetized by heating of these precursors in air and other atmospheres, such as argon, hydrogen, and nitrogen [1], but only a few papers studied the influence of the atmosphere on its structural, textural, optical, and photocatalytic properties .

The aim of this work was to synthetise g-C_3N_4 in the argon atmosphere and to study its physico-chemical, textural, and morphological properties. The prepared materials were characterized by common techniques and the presence of vacancies was investigated by positron annihilation spectroscopy. The materials were used for the photocatalytic evolution of hydrogen. The best photocatalyst showed 3 times higher performance (1547 µmol/g) than bulk g-C_3N_4 synthetized in the air (547 µmol/g) [2].

Acknowledgments
This work was supported by the Czech Science Foundation (project No. 19-15199S), Visegrad Fund (project No. 8F21007). The authors also thank the Large Research Infrastructure ENREGAT (project No. LM2018098). Computational resources for ab-initio calculations were supplied by the project "e-Infrastruktura CZ" (e-INFRA LM2018140) provided within the program Projects of Large Research, Development and Innovations Infrastructures.

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Simultaneous oxidative and reductive transformations by parallel catalysis with N-Heterocyclic Carbenes

Nadhrata ASSANI, Ludivine DELFAU, Eder TOMAS-MENDIVIL, Sébastien REDON, Patrice VANELLE, David MARTIN,[1] Julie BROGGI[2]

[1]*Aix-Marseille Université , Marseille, France*

[2] *Univ. Grenoble-Alpes, Grenoble, France*

[*]julie.broggi@univ-amu.fr, david.martin@univ-grenoble-alpes.fr

The last decade, a multitude of organocatalyzed transformations of carbonyl derivatives took advantage of the oxidation of Breslow intermediates, arising from the reaction of these carbonyl substrates with stable N-Heterocyclic Carbenes (NHCs). However, valorization of the electrons lost during these oxidative transformations had not been addressed until recently. In 2021, Ohmiya and Bertrand independently demonstrated that these Breslow intermediates can also be used as formal reductants.[1][2] NHC-organocatalyzed arylacylations of diverse alkenes were thus performed upon reduction of iodoaryl derivatives into radical species. In their reaction, the aldehyde used to generate the Breslow enaminol was also integrated in the final addition product.

Our goal was to develop a system enabling the use of aldehydes as sources of potent Organic Electron Donors (OEDs) for reductive transformations in organic chemistry.[3][4][5] Our strategy allows the coexistence of two distinct and interdependent catalytic cycles where the Breslow enolate catalyst both serves as an electron source for reduction reactions and as key intermediate for the valorization of aldehydes through oxidative transformations. Imidazolylidene-based enaminols proved to be powerful organic donors for the single-electron transfer reduction of various challenging substrates. The generated radical intermediates were further exploited in arylations of alkenes while the sacrificial aldehydes were valorized through oxidation reactions.

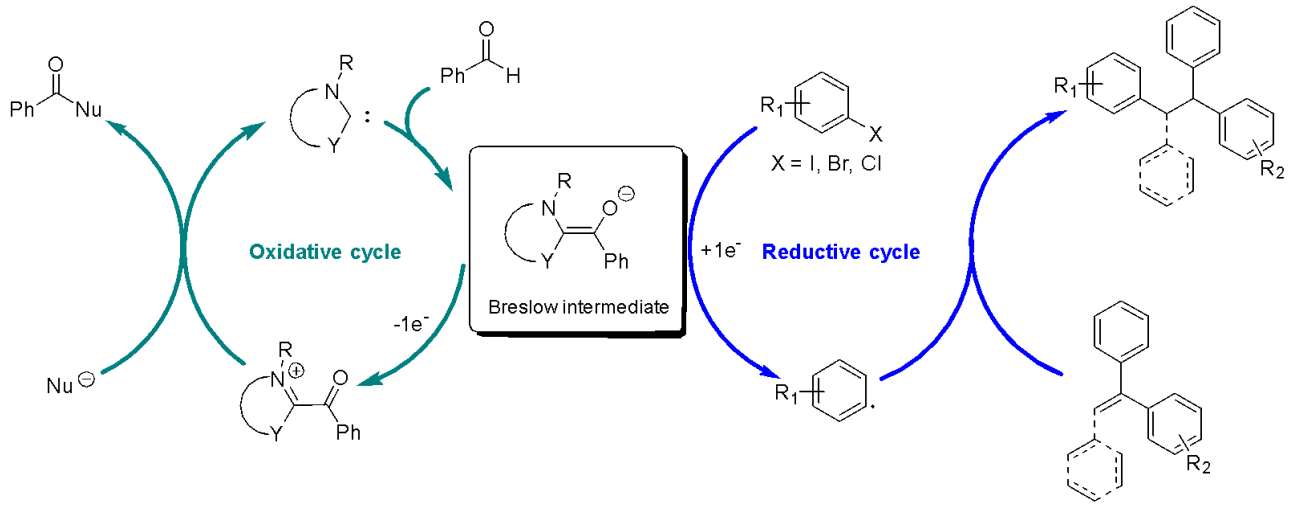

Figure 1 - Proposed mechanism for the concomitant oxidative and reductive transformations

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Cation-induced Speciation of Port-Size in MOR Zeolite Synthesis

Sebastian Prodinger[1*], Odd Reidar Bygdnes[1], Izar Capel Berdiell[1], Tomas Cordero-Lanzac[1], Bjørn Gading Solemsli[1], Karoline Kvande[1], Pablo Beato[2], Unni Olsbye[1], & Stian Svelle[1]

[1] *Center for Materials Science and Nanotechnology (SMN), Department of Chemistry, University of Oslo, 1033 Blindern, 0315 Oslo, Norway*

[2] *Haldor Topsøe A/S, Haldor Topsøes Allé 1, 2800 Kongens Lyngby, Denmark*

[*] *sebastian.prodinger@smn.uio.no*

Keywords: Cations, Zeolite formation, Mordenite, port-size

Introduction. The mordenite framework is one of the handful of synthetic zeolite structures used extensively in petrochemical industrial applications. Classified as a large-pore zeolite (12-rings) it also contains a small-pore side pocket that can only be accessed via the 12-ring. The side-pocket has been shown to be crucial to small-molecule activation such as methane to methanol oxidation and DME carbonylation, driven in part by the spatial distribution of Al.[1] Interestingly, MOR also exists in two variants depending on the aperture size of the pore opening (i.e. port size), defined by the extent of benzene adsorption as noted by Sand as early as 1968.[2] Various hypothesis have been proposed over the years, among which cation location and dealumination suggest a link to Al distribution.[3] Here we report, for the first time, a single-parameter study leading to the successful variation in port size based solely on a synthesis approach.

Experimental/methodology. Zeolite synthesis was based on a modified approach reported by Chi & Sand.[4] We systematically varied the Na/K ratio in the gel by substituting NaOH for KOH (85%), maintaining all other parameters. Material characterization was accomplished with a suite of tools such as X-ray diffraction, N_2-physisorption, scanning electron microscopy, elemental analysis, and temperature programmed desorption using propylamine and NH_3. The port size was determined performing a toluene breakthrough experiment. Catalytic testing involved propene oligomerization and isobutane cracking.

Results and discussion. We successfully synthesized a range of MOR zeolites containing increasing fractions of K^+ in the gel (Figure 1). All materials crystallized at 185 °C. As the fraction of K^+ ions in the gel increased, both the induction period and the crystallization period slowed down requiring a longer time to achieve full crystallinity. When probing the protonic forms with toluene vapors (as benzene substituent) we found that the uptake becomes limited once the K concentration reaches a certain threshold (K/Na > 0.75 in MOR). Performing a temperature programmed desorption step of the adsorbed toluene allowed us to deduce that the pore size is slightly smaller in the K-MOR system. While we previously used propylamine TPD to determine the accessibility of acid sites in MOR, we find here that this descriptor seems to also correlate with propene oligomerization in the pores, with more extensive propene coking in the small-port K-MOR system. This is further supported by reactivity tests with propene and isobutane performed in a fixed bed reactor. Rietveld refinement of X-ray diffraction data highlights the spatial differences in the Na^+ and K^+ distribution of the crystallized MOR systems, which ultimately leads us to conclude on the cation-induced speciation of the MOR port-size. This promises to resolve a long-standing question related to this highly relevant, industrial catalyst.

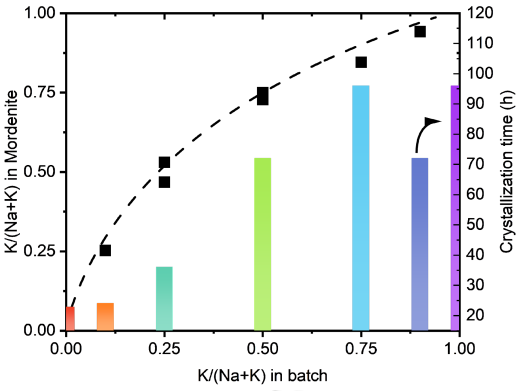

Figure SEQ Figure * ARABIC 1. Crystallization time and K^+ content for the synthesized MOR zeolite as a function of K^+ content in the gel.

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A Review on Electron-Hole Pairs Mechanism in Dark Photocatalysis

Jouvan Chandra Pratama Putra[1*], Tore Sandnes Vehus[1], Henrik Kofoed Nielsen[1]

[1]*Department of Engineering Sciences, University of Agder, 4879 Grimstad, Norway*
**jouvan.c.putra@uia.no*

Keywords: dark photocatalysis, trapping and releasing electron-hole pairs, indoor air quality, catalyst.
Fundamentally, catalyst for photocatalysis process requires a light source to produce electron-hole pairs [1] and it is a major challenge to implement this system to reduce indoor air pollutants continuously without having optimal light available continuously too. Band gap engineering may be a promising technique for adjusting energy required to meet the variation of light sources such as ultraviolet light, visible light, and near infrared light to activate the catalyst [2], [3]. The number of electron-hole pairs produced during irradiation varies depending on the light sources [4]. Therefore, it is possible to generate large amount of the pairs and the excess number of pairs can be stored in the photocatalysis material to be released at night. This mechanism can be adopted to overcome the limitations of the traditional photocatalysis and is known as dark photocatalysis which has two main processes such as harvesting and releasing of light energy [5]. The aim of this review paper is to propose an innovative mechanism to degrade indoor air pollutants around the clock. A general overview of the trapped and released electron-hole pairs is presented. Finally, the potential challenges in the further application of dark photocatalysis are discussed as an efficient indoor air purification technique.

Acknowledgments
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Kinetic investigation of NH_3 decomposition over Ru-based catalysts

Y. Qiu[1], F. Franchi, N. Usberti, M. Ambrosetti, G. Groppi, E. Tronconi, A. Beretta[1*]

[1]*Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via Lambruschini 4, 20156, Milano, Italy*
[*]*alessandra.beretta@polimi.it*

Keywords: Hydrogen carrier, hydrogen production, ammonia decomposition, kinetic investigation

Introduction.
To achieve net-zero CO_2 emission in the coming decades, hydrogen is considered as one of the most promising energy carriers for the future energy systems [1]. To overcome the challenges for the storage and transportation of H_2, the generation of CO_x-free hydrogen from ammonia decomposition has attracted increasing attention, since NH_3 has high volumetric energy density (108 kg-H_2/m^3 NH_3 at 20 °C and 8.6 bar) and gravimetric energy density (17.8 wt.%), combined with its ease of storage and transportation [2]. According to the state of the art, Ru is the most active metal for NH_3 decomposition [3]. Although widely studied, the mechanism and kinetics of NH_3 decomposition over Ru-based catalysts are still discussed and fertile soil of new findings. In this work, a kinetic investigation of NH_3 decomposition was performed over home-made Ru-based catalysts. The effects of the main operating conditions (temperature, space velocity, feed composition) were systematically studied aiming at the identification of the prevailing kinetic dependences and a better understanding of the mechanism and rate controlling factors.

Experimental/methodology.
1% Ru/ Al_2O_3 (Cat. A) and 1% Ru/ MgO (Cat. B) catalysts were prepared via an incipient wetness impregnation by using $RuCl_3$ as precursor. Catalytic tests were carried out in a continuous fixed-bed flow reactor, after reduction in flowing H_2 at 450 °C. NH_3 decomposition was tested at varying gas hourly space velocity and ammonia concentration, from ppm to highly concentrated feeds. H_2 and N_2 co-feed exepriments were also performed. Product gas composition was analyzed by on-line MS.

Results and discussion.

The catalytic performance of catalysts Cat. A and Cat. B under selected feed conditions are compared in Figure 1. Results showed a negative effect of NH_3 feed concentration over conversion, suggesting a global kinetic order lower than 1. When co-feeding large quantities of H_2, NH_3 conversion dropped importantly and the conversion curves were shifted to much higher temperatures; this clearly suggests that H_2 adsorption strongly inhibits NH_3 activation on Ru. Additional tests showed that under large H_2-cofeed, the process gain a full first order dependence on NH_3 and conversion become independent on NH_3 content from low to very high concentrations (not reported). A Langmuir-Hinshelwood kinetic model can nicely describe the observed effects, assuming that H is MASI and that the rate determing step lies within the dehydrogenation path of NH_3 rather than the associative desorption of products.

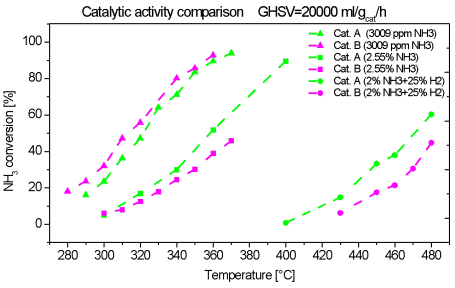

Figure 1. Catalytic activities comparison between catalyst 1% Ru/Al_2O_3 and 1% Ru/MgO, GHSV = 20000 Nl/kg/h.

The comparison between the two catalyst formulations showed however that the strength of NH_3 and H_2 inhibition have different intensity due to the nature of catalyst supports. Dynamic experiments reveal in fact differences of strength of adsorption and coverage of surface species.

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Fabrication of Pd-supported 3D printing activated carbon monoliths for hydrogen production

G. Vega[1], I. Díaz-Herrezuelo[2], M. Navarro[1], A. Quintanilla[1], M. Belmonte[2] and J.A. Casas[1]

[1]*Department of Chemical Engineering, Universidad Autónoma de Madrid, Spain, Madrid, Spain*
[2]*Institute of Ceramics and Glass (ICV-CSIC), Madrid, Spain*
[*]*Corresponding Author's E-mail address: gonzalo.vega@uam.es*

Keywords: 3D printing, Hydrogen production, LOHC, Formic acid dehydrogenation, Monolithic catalysts

Introduction. The use of a liquid organic hydrogen carriers (LOHCs) has shown to be a safe, practical, and economic alternative for hydrogen (H_2) storage and transportation. Among them, formic acid (FA) is a probable candidate considering its high volumetric H_2 capacity and low toxicity [1]. The most efficient solid catalyst for the FA dehydrogenation reaction is Pd nanoparticles on activated carbon (AC) supports [2]. In this work, a catalyst consisting of supported Pd nanoparticles on robust and porous AC monoliths fabricated by 3D printing is developed and applied in the continuous production of H_2 from FA dehydrogenation reaction.

Experimental/methodology. Different compositions of AC powders (>100 nm particle size, Merck) and a colloidal dispersion of boehmite (41 wt.%) were mixed to prepare printable water-based inks. The inks were extruded with a three-axis robocasting system to fabricate cylindrical monoliths with square cells. The as-printed monoliths were heat-treated at 1300 ºC in a vacuum furnace for 30 min, resulting in 3D monoliths made of AC and Al_2O_3. Pd nanoparticles were immobilized on the 3D AC monoliths by the wetness impregnation method, using $PdCl_2$ as a precursor, followed by reduction in a gas stream (H_2:N_2= 50; 100 NmL/min) at 250 ºC for 2 h. The FA dehydrogenation experiments were carried out in an up-flow tubular reactor at: $C_{FA,0}$=[0.5-1] M, T=[25-55] ºC, Q_L= 0.25 mL min^{-1}, Q_{He}=17 mL min^{-1} as a carrier gas, W_{CAT}=2.4 g (5 monolith pieces) and τ=160 g h L^{-1}.

Results and discussion. Figure 1a shows an image with the dimensions of the 3D Pd/AC monolithic catalyst where the shape of the open channels and filaments is preserved. The average size of the Pd nanoparticles was 1.9 ± 0.4 nm, which were homogeneously distributed on the scaffold surface, as was observed by SEM analysis (data do not shown). The atomic ratio Pd^{2+}/Pd^0 was 1.4 and the content of Pd was 4.8 wt.%, measured by XPS and TXRF, respectively. As expected by the physical and chemical properties of the supported Pd nanoparticles, the 3D Pd/AC monoliths exhibited high catalytic activity in the FA dehydrogenation reaction (see Figs. 1b and c) yielding only H_2 and CO_2 (with H_2/CO_2 ratio= 1-1.2). Under reaction conditions, FA conversions (X_{FA}) between 80 and 90% were achieved and gas produced flow rates were as high as 12 NmL/min. After a given period of time on stream, the 3D Pd/AC catalyst deactivates, particularly at high temperatures and initial FA concentration (Fig. 1c).The catalyst activity can be restored by drying the monoliths in air at 60 ºC for 24 h. These results demonstrate that structured catalysts such as 3D Pd/AC are promising candidates for the continuous production of CO-free H_2 using FA as carrier.

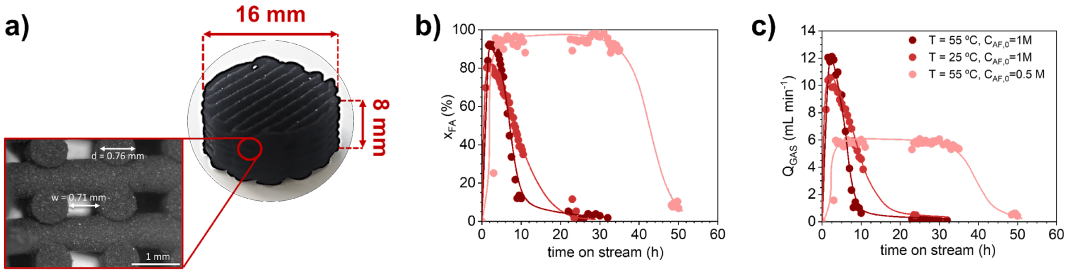

Figure 1. (a) Photograph of a 3D 5wt.%Pd/CA monolith; (b) temporal profiles for FA conversion (x_{FA}) and (c) gas flow produced.

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Carbon nanotube-supported bimetallic catalysts with high activity for the reduction of NOx

P.S.F. Ramalho[1,2*], O.S.G.P. Soares[1,2], J.L. Figueiredo[1,2], M.F.R. Pereira[1,2]

[1] *LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.*
[2] *ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.*
*E-mail: psfr@fe.up.pt

Keywords: Nitric oxide, catalytic reduction, SCR, carbon nanotube, copper, potassium

Introduction.

The reduction of nitrogen oxide (NO_X) emissions is one of the main environmental concerns, as they can cause global warming, acid rain, the greenhouse effect, and several problems for human health. Thus, it is imperative to develop advanced technologies and catalysts to control NO_X emissions to comply with increasingly stringent legislation [1].

Selective catalytic reduction is a means of converting NO_X with the aid of a catalyst into N_2. At low temperatures, carbon-based catalysts show greater catalytic activity in reducing NOx than conventional catalysts; therefore, selective catalytic reduction with carbon (SCR-C) is an excellent alternative for NOx reduction, with the additional advantage of avoiding the need for an external reducing agent [2]. Recent studies have shown that NO can be reduced to N_2 at temperatures below 500 °C, using carbon materials impregnated with transition metals or metallic oxides [3].

The main objective of this work is to study the reduction of NO using carbon nanotubes (CNT) as a catalyst or as a support for the metallic phases.

Experimental/methodology.

Two different supports were used for the incorporation of the metallic phase by incipient impregnation with copper or potassium: the original (CNT) and the nitrogen-doped (CNT_M_BM) samples. The textural and chemical properties of the materials were characterized by N_2 adsorption at -196 °C, inductively coupled plasma-optical emission spectrometry (ICP-OES), and elemental analysis (EA).

NO reduction experiments were performed in a fixed-bed, U-shaped flow reactor. The mass of the sample was 0.2 g, the flow rate was 100 $cm^3\ min^{-1}$, and the concentration of NO in He was 1000 ppm.

Results and discussion.

Carbon nanotubes (CNT) do not show significant catalytic activity in the reduction of NO. When incorporating copper the performance is a little better, obtaining a conversion of 26%. The introduction of nitrogen surface groups (CNT_M_MB) further increases the catalytic activity, thus observing that the nitrogen incorporated into carbon nanotubes increases their catalytic activity, thus showing a NO reduction of 78%. In this work, the effect of adding potassium to copper on both types of support for the reduction of NO was investigated and it was verified that the addition of potassium significantly improves its catalytic performance. Among the samples, the best results were obtained for copper supported on nitrogen-doped CNT and impregnated with potassium (CNT_M_BM@CuK), obtaining a NO reduction of 100% for a T = 360 °C.

Acknowledgements

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Ru@C microspheres for Photo-Thermal catalysis applications

A. Rendón-Patiño[1*], D. Mateo[1], E. V. Ramos-Fernandez[2*] and J. Gascon[1*]

[1]*King Abdullah University of Science and Technology, Thuwal, Saudi Arabia*
[2] *Universidad de Alicante, Alicante, Spain*
[*]*alejandra.patino@kaust.edu.sa*

Introduction. Photothermal catalysis is a hybrid approach that combines the advantages of photocatalysis and thermocatalysis. [1] In this regard, carbon-based materials are promising candidates for applications in photothermal catalysis due to their broad light absorption and effective light-to-heat conversion. Furthermore, metal nanoparticles are also considered excellent nano-heaters so the combination of both elements can be crucial to improve the photo-thermal performance. With this in mind, in this work we have designed a novel photothermal catalyst based on Ru nanoparticles encapsulated within carbon microspheres (Ru@C).

Experimental/methodology. For the synthesis of these materials, 4 mL of 0.02 M K_2RuCl_5 solution were added drop by drop to a 40 mL 0.5 M glucose solution under vigorous stirring. [2] Then, the mixture was transferred into a 50 mL Teflon-sealed autoclave and maintained at 160 °C for 2 h. The puce powder was recovered by filtration, washed with ethanol and water several times, and oven-dried at 70 °C overnight. Ru@C microspheres were finally pyrolyzed at 300-700°C for 2 h under N_2 atmosphere. All the samples were characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), elemental mapping using Energy Disperse X-Ray (EDX), Raman spectroscopy, Elemental Analysis (EA), Inductively Coupled Plasma (ICP), Thermogravimetry (TGA), and X-ray Photoelectron Spectroscopy (XPS).

Results and discussion. STEM images revealed that the nanoparticles of ruthenium are encapsulated within the carbon microspheres, displaying a range of sizes between 1 to 20 nm (Figure 1a). Moreover, according to SEM images, the carbon microspheres show diameters ranging from 0.2 to 8 μm (Figure 1b). The content of Ruthenium was determined by ICP analysis, obtaining an estimated amount of 0.5 %. The nature of carbon spheres was also characterized by Raman spectroscopy and XPS. The Raman spectra showed the expected G band at 1590 cm^{-1} accompanied by a D band at 1350 cm^{-1} that is associated with the presence of defects. Survey XPS analysis indicates that the deconvolution of the C1s presented a significantly larger contribution of Carbon sp^2. In view of these results, the as-prepared carbon microspheres with encapsulated ruthenium nanoparticles are expected to present a good photothermal performance combining the efficient light-to-heat capabilities of both elements.

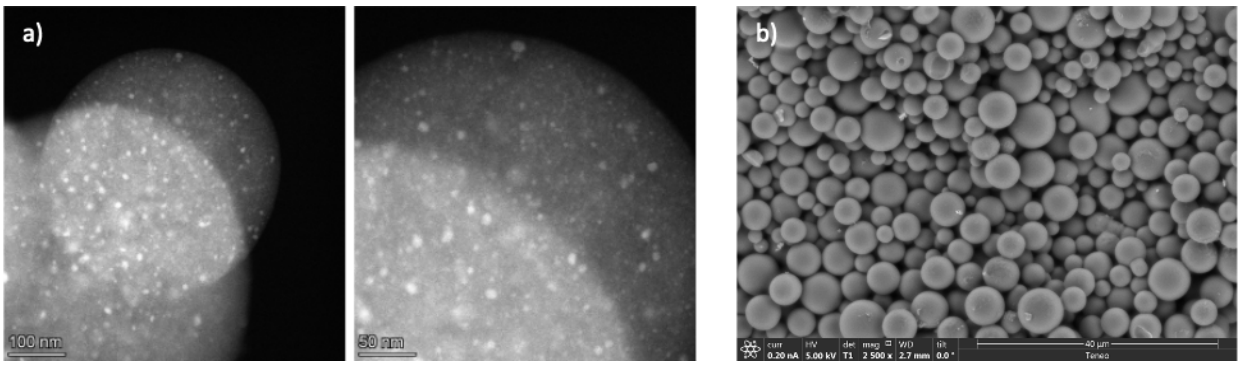

Figure 1. (a) STEM and (b) SEM images of Ru@C microspheres.

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Atomically dispersed platinum supported in FeO_x/SiO_2 for the selective non-oxidative dehydrogenation of isobutane

A. Rodriguez-Gomez,[1,2]* S. Ould-Chikh,[1] W. Henao,[2] G. Agostini,[3] G. Prieto[2] and J. Gascon[1]
[1]*King Abdullah University of Science and Technology, KAUST Catalysis Center, Thuwal, Saudi Arabia*
[2] *Instituto de Tecnología Química, Universitat Politècnica de València-CSIC, Valencia, Spain*
[3]*ALBA Synchrotron Light Source, Barcelona, Spain*
[*]*arodgom@itq.upv.es*

Introduction. For decades, Pt and CrO_x have been the most commercialized catalysts in the non-oxidative dehydrogenation of alkanes by on-purpose technologies (UOP Oleflex/Lummus Catofin). The UOP commercial catalyst contains ca. 0.3 wt.% of Pt supported on alumina and promoted with Sn and alkaline metals. The temperatures to which the catalytic converter is subjected lead to the sintering of the active phase and coke formation. This depresses catalytic activity in few hours, requiring a complex regeneration process which involves coke gasification and Pt re-dispersion.[1,2] Several alternatives have been proposed to modify the physicochemical properties of Pt in order to improve its stability and selectivity in the dehydrogenation of alkanes. Among them, the suitability of Fe as an additive has been highlighted due to its influence on the electronic properties of Pt, with a shift of the d-band center towards the Fermi level, weakening the adsorption of alkenes and avoiding further transformations.[3] In this work, we have studied a series of Pt-Fe catalysts supported on SBA-15 for the non-oxidative dehydrogenation of isobutane. The high specific surface area of mesostructured silica allowed a high dispersion of the supported bimetallic phase thus generating small clusters/nanoparticles after a reduction pre-treatment in hydrogen at 600 °C.

Experimental. (*i*) Catalyst preparation: a series of Pt-Fe bimetallic catalysts were prepared by ultrasound-assisted co-impregnation of the metal precursors (H_2PtCl_6 +$Fe(NO_3)_3$) on a mesostructured SBA-15 support for different metal loadings and Pt/Fe ratios (Pt<<<Fe), dried at 110 °C for 16 h and calcined in a muffle for 3 h at 550 °C. (*ii*) Characterization: as-prepared catalysts were analyzed by XRD, TPR and Eletron Tomography. Next, pre-reduced catalytic systems were characterized by STEM-HAADF+EDS mapping and XAS (Fig. 1a and 1b, respectively) to determine the chemical environment of Pt on the FeO_x/SBA-15 matrix. (*iii*) Catalytic studies: the sized catalysts (150-250 μm) were tested in the non-oxid ative dehydrogenation of isobutane at atmospheric pressure (P_{iC4H10}=0.05 MPa) in a tubular quartz reactor (Ø=8 mm) in fixed-bed mode at 550 °C. Recyclability tests were carried out by subjecting the spent catalyst to consecutive reaction-regeneration cycles (regeneration conditions: 2% O_2 stream, heating ramp=2 °C·min^{-1}).

Results and discussion. Structural characterization of the calcined catalysts determined the preferential presence of the hematite phase (XRD) within the mesoporous channels of SBA-15 (Tomography). TPR profiles suggested the formation of bimetallic Pt-Fe phases at low temperature as well as hardly reducible iron silicates. TEM confirmed the high dispersion of the pre-reduced Fe phase in the bimetallic systems (< 5 nm particles) and the homogeneous distribution of Pt on the Fe matrix which appears to be atomically dispersed within an Fe matrix (see Fig.b right, EXAFS analysis). These characteristics seem to be responsible for its high activity (X_{iC4H10}=43%, S_{iC4H8}=96%) and stability in the dehydrogenation of isobutane.

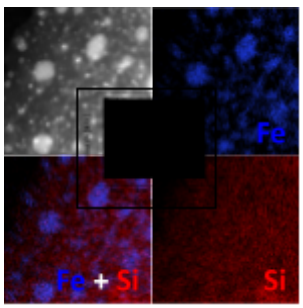

Table 1. Activity on the dehydrogenation of iC_4H_{10} at 550 °C after TOS=10 hours.

Catalyst (**x**Fe**y**Pt)/SBA-15	X_{iC4H10}	S_{iC4H8}	$C_{balance.}$ (gas phase)
10Fe-	20	82	94

0.1Pt-	9	82	98
0.01Pt10Fe-	20	89	97
0.1Pt10Fe-	43	96	>99
0.5Pt10Fe-	49	94	99

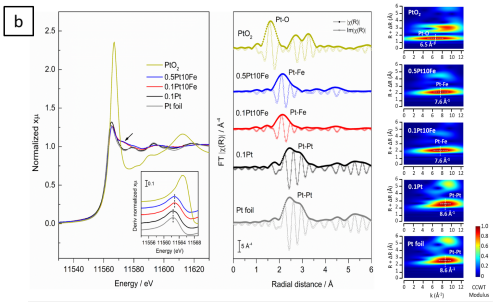

Figure 1. Dark-field HAADF-STEM + EDX mapping of 0.5Pt10Fe/SBA-15 (a) and XAS analysis of the xFeyPt/SBA-15 catalysts (b).

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Development of Stable Ceria-Supported Noble Metal Catalysts with Sulfur Resistance for Waste-to-Hydrogen

H.-S. Roh[1*], K.-J. Kim[1], S.-J. Ryu[1]

[1]*Department of Environmental and Energy Engineering, Yonsei University, 1 Yonseidae-gil, Wonju, Gangwon 26493, Republic of Korea*
[*]*hsroh@yonsei.ac.kr*

Introduction. Waste-to-hydrogen technology is being proposed to solve the problem caused by the increasing amount of waste in worldwide. From the perspective of waste-to-hydrogen, waste gasification can obtain gaseous products (CO, H_2, CH_4, and CO_2) from waste. In our preceding study, we have been tried to establish an eco-friendly method for H_2 production through waste gasification combined with the high-temperature water-gas shift (HT-WGS, $CO + H_2O \leftrightarrow H_2 + CO_2$, ΔH = -41.2 kJ/mol) reaction [1-2]. However, impurities such as sulfur are partly contained in waste-derived synthesis gas, which act as a poison to the catalyst in the HT-WGS reaction [3]. Therefore, we aimed to develop a highly active and sulfur-tolerant catalysts for the conversion of waste-derived synthesis gas.

Experimental/methodology. CeO_2-supported catalysts with various noble metals (Pt, Rh, Ru, and Pd, 2 wt% each) were prepared by the incipient wetness impregnation method. The intrinsic catalytic activity of the prepared catalyst was tested at 400 ℃ for 18 h, and sulfur resistance of the catalyst was evaluated by injecting 500 ppm of H_2S during the WGS reaction. The physico-chemical properties of the CeO_2-based catalysts were characterized using various techniques such as Brunauer-Emmett-Teller surface area and pore analysis, X-ray diffraction, H_2-temperature programmed reduction, X-ray photoelectron spectroscopy, H_2-O_2 pulse reaction, CO−chemisorption, Photoluminescence, high-angle annular dark-field scanning transmission electron microscopy and energy dispersive X-ray spectroscopy.

Results and discussion. In our previous research, among the various support candidates such as CeO_2, ZrO_2, MgO, and Al_2O_3, CeO_2-supported catalyst exhibited the best sulfur resistance and regeneration rate due to the superior redox property and high oxygen storage capacity of CeO_2, which accelerates the redox mechanism of HT-WGS [3]. In this study, Various noble metals (Pt, Rh, Ru, and Pd) were supported on CeO_2 to understand their sulfur-tolerant catalytic activity. Among the samples, the Pt-based catalyst showed the highest sulfur tolerance and recovery of catalytic activity. Considering the catalytic reaction results and physicochemical properties, the sulfur tolerance of the catalyst is affected by oxygen vacancies and redox properties, which are closely related to the interaction between the metal and the CeO_2 support. In addition, the oxygen storage capacity concentration was used as an indicator for classifying the recovered catalyst and the non-recovered catalyst which had been poisoned by sulfur.

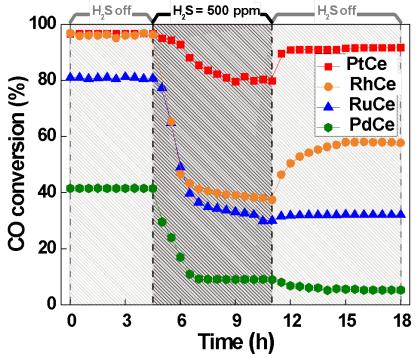

Figure 1. Catalytic performance with time on stream over CeO_2-supported catalysts with various noble metals ($H_2O/(CH_4 + CO + CO_2)$ = 2.0; GHSV = 46,000 h^{-1}; T = 400 ℃).

Catalyst	Oxygen storage capacity (10^{-4} gmol/g_{cat})
PtCe	4.68
RhCe	4.53
RuCe	4.52
PdCe	4.17

Table 1. Oxygen storage capacity-related values of CeO_2-supported catalysts with various noble metals.

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Co_3O_4@SiO_2 yolk-shell catalysts for total oxidation of toluene

Anna Rokicińska*, Magdalena Żurowska, Bazyli Olszański, Marek Dębosz, Piotr Kuśtrowski

Faculty of Chemistry, Jagiellonian University, Krakow, Poland
**anna.rokicinska@uj.edu.pl*

Keywords: catalytic combustion of volatile organic compounds, Co_3O_4 catalysts, core-shell structures

Introduction. Core-shell structures are a new class of nanostuctured materials that have been attracting increasing interest in recent years due to their attractive properties and possible applications. The design of such materials, based on bottom-up or top-down strategies, gives the opportunity to produce catalysts with various physicochemical features dedicated to selected catalytic reactions [1,2]. Their catalytic activity often depends on the synergistic interactions between a core and a shell. However, the great advantage of the presence of the shell is also the protection of the active phase against sintering and the creation of a nanoreactor space for the catalytic reaction to take place. In this approach, an interesting idea may be yolk-shell structures containing highly dispersed nanoparticles of an active phase enclosed inside a mesoporous shell that guarantees relatively easy transport of reagents [3]. In the presented work, Co_3O_4@SiO_2 yolk-shell systems were developed for the elimination of volatile organic compounds (VOCs) from polluted air by the catalytic combustion.

Experimental. Spherical particles of diethyltriamine-functionalized poly(maleic anhydride) (MA-DETA) and polystyrene (PS) with uniform diameters within the range of 200-240 nm were synthesized. Subsequently, the polymer template was surrounded by a SiO_2 precursor using the modified Stöber strategy. An influence of type of solvent, amount of SiO_2 precursor, TEOS/NH_3 ratio and addition of surfactant on quality of the formed coatings was tested using scanning electron microscopy (SEM). As the result of optimization of SiO_2 deposition, the spherical silica materials with high specific surface area (S_{BET} value above 1100 m^2/g) were obtained, containing mesopores enabling access to their interior. In the next step of the synthesis, a transition metal oxide (i.e. Co_3O_4) precursor was incorporated into the polymer@SiO_2 materials using various approaches, including wet impregnation and adsorption process. The kind of modification method and the amount of the introduced Co_3O_4 precursor determined properties of the active phase created within the yolk-shell structures after the polymer core removal by calcination at the oxidizing atmosphere. The structure, composition and reducibility of the Co_3O_4-containing materials were studied by XRD, XRF, UV-Vis-DR, XPS and H_2-TPR. Moreover, the synthesized catalysts were tested in the combustion of toluene.

Results and discussion. The nanostructures containing catalytically active Co_3O_4 spinel nanoparticles surrounded by mesoporous SiO_2 shells were formed. In comparison to conventional catalysts that contain the Co_3O_4 active phase deposited on a SiO_2 support, the proposed yolk-shell structure provides a better access of reactants to the surface of active phase nanoparticles, which results in their higher activity and selectivity in the VOCs combustion. The kind of the polymer template used for the synthesis of the SiO_2 spheres had a significant impact on the catalytic activity. The catalysts prepared on the basis of the MA-DETA template were characterized by significantly better catalytic activity compared to those constructed on the PS grains. The differences in the catalytic activity were related to the dispersion of Co_3O_4 nanoparticles inside the silica spheres. The high dispersion obtained in the case of using the MA-DETA matrix resulted from the presence of amino groups, which ensured the appropriate adsorption capacity of Co^{3+} ions introduced during the modification. As a result, extremely active systems were achieved, far exceeding those described in the scientific literature.

Acknowledgments
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Reactivity and stability of spinel oxides for the aqueous catalytic oxidation of alcohols in batch conditions

F. Romanelli[1,2], A. Tampieri[1], T. Lederer[1], M. Pittenauer[1], K. Föttinger[1]*

[1]*Institute of Materials Chemistry, Technische Universität Wien, Vienna, Austria*
[2]*Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Milan, Italy*
**karin.foettinger@tuwien.ac.at*

Keywords: Spinel oxides, alcohol oxidation, batch reactor, kinetic study.

Introduction. The chemical industry relies on the selective oxidation of alcohols to aldehydes or ketones as a powerful and versatile transformation step for the synthesis of valuable compounds. Aldehydes and ketones are important intermediates in the synthesis of pharmaceutically active agents, antioxidants, agrochemicals and fine chemicals. While small alcohols are selectively oxidized in well-established industrial processes, the selective oxidation of higher alcohols still leaves room for improvement. The most active catalysts for this reaction are based on noble metals [1]. Metal oxide catalysts, despite being more complex and having less defined active sites, are based on abundant metals and are less prone to leaching. Hence, the exploration and design of highly active and selective oxide catalysts for alcohol oxidations plays a relevant role in promoting more environmentally sustainable synthesis paths for a wide range of organic molecules.

Experimental/methodology. The spinel oxide catalysts, based on Mn, Fe, Co, Ni, Cu, and Zn and with different compositions, were prepared via combustion synthesis and calcination. The synthesised solids were tested as catalysts for the liquid phase oxidation of alcohols, such as isopropanol and 2-butanol, to ketones (acetone and 2-butanone, respectively) in a 300 mL autoclave reactor. The catalyst powder was suspended by magnetic stirring in an aqueous solution of the alcohol. The suspension was pressurised with oxygen at different pressures (up to 50 bar) and heated at different temperatures (160-250°C). For each set of operating conditions, after different operating times, the composition of the liquid was determined by GC-FID. Both fresh and used catalysts, after the reaction and hydrothermal treatments, were characterised by XRD, N_2-physisorption, SEM-EDX, XPS, and FT-IR.

Results and discussion. The reaction rates were determined upon regression of experimental data. Co_3O_4 was used as the model catalyst, and the composition was modified to assess the influence of metal substitution and structure modifications on the catalytic activity and selectivity. The catalytic results obtained with batch conditions were compared to the ones obtained in flow. The characterisation results allowed to investigate changes in crystalline phases, catalyst surface and morphology due to exposure to reaction conditions.

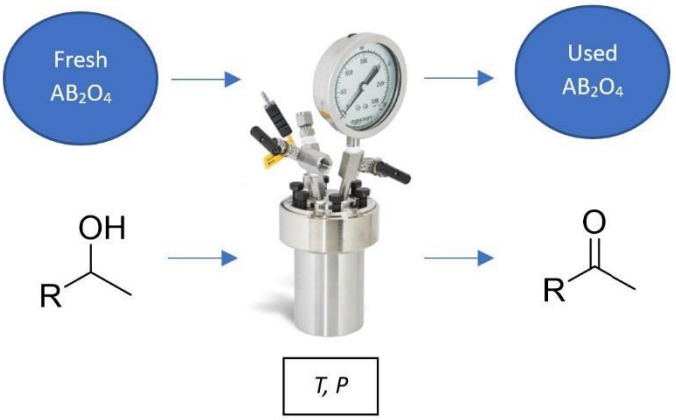

Figure 1. Figure 1. Catalytic testing of different spinel oxides for the selective oxidation of alcohols to ketones.

Acknowledgments
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Carbon vs. conventional supported catalysts for CO_2 utilization

S. E. Atakoohi[1], E. Spennati[1], P. Riani[2], G. Garbarino[1]*

[1]*Department of Civil, Chemical, and Environmental Engineering, University of Genoa, Genoa, Italy*
[2]*Department of Chemistry and Industrial Chemistry, University of Genoa, Genoa, Italy*
**gabriella.garbarino@unige.it*

Keywords: Graphene nanoplatelets, CO_2 methanation, carbon-supported catalysts

Introduction. CO_2 emission from fossil fuel combustion is one of the most common causes of global warming. The catalytic hydrogenation of CO_2 to methane is an efficient way to reduce CO_2 emissions. As an example, among noble and transition metals, supported nickel and ruthenium catalysts are the most promising candidate for CO_2 methanation reaction; nickel is sometimes preferred for its high activity and relatively low cost [1]. However, the role of support plays a central role in the activity and stability of the synthesized catalysts. Ni catalysts are generally supported on various oxides such as Al_2O_3, SiO_2, ZrO_2, and CeO_2 with quite variable loadings (5-50 wt.%) and suitable promoters. Carbon-supported catalysts are timely of interest for different green chemistry reactions and according to our previous work efficiently support cobalt nanoparticles in Ethanol Steam Reforming reaction [2]. As well, graphene, which possesses unique properties, has been already used to disperse monometallic and bimetallic nanoparticles, showing remarkable catalytic performances in many reactions. However, studies that use graphene as catalyst support in the heterogeneous catalysis field are still limited [3]. Conventional graphene production is mainly related to the Hummers' method and recently different other preparations have been attempted [4]. In this work, a green and sustainable process using the molten salt method has been applied to produce high-quality Graphene nanoplatelets (Gnp) to evaluate their possible use in the frame of CO_2 utilization reactions by comparing their activity with conventional and carbon nanotube-supported catalysts.

Experimental/methodology. Graphite powder has been used as the precursor to synthesize graphene using a molten salt method proposed by E. Ruse et al. [5]. Synthesis has been here optimized by also evaluating the possible recycling of used salts in the optic of circular economy approach. Briefly, graphite powder was mixed with a eutectic salts mixture (NaCl/KCl) with a graphite/salt ratio of 1:9. The graphite-salt mixture was then heated in an Ar atmosphere with a rate of 10 K min^{-1} to 1023 K and kept for 360 min. After cooling down Gnp was recovered. Carbon nanotube-supported catalysts have been synthesized following the preparation procedure reported in the open literature [6] and as a reference, Ni and Ru/Al_2O_3 catalysts have been prepared for comparison purposes. Following our previous work [7], CO_2 hydrogenation experiments are actually under evaluation. Online products analysis will be performed using an FT-IR instrument.

Results and discussion. At the present, graphene nanoplatelets were successfully produced with a yield of 30-40 wt.% following molten salt procedure and, conversely supported Ni- over carbon nanotubes have been produced optimizing preparation parameters. Characterization by SEM, XRD, and FT-IR confirmed the achievement of desired products both for carbon-based and supported catalytic materials (Ni/Al_2O_3 and Ru/Al_2O_3). At the present, the optimization of metal introduction and possibly single-atom rational catalyst design are under deep investigation together with the evaluation of the catalytic activity.

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Zeolite-Templated Carbon Metal-Supported Catalysts for Heterogeneous Reactions

Petr Sazama[1,*], Vasile I. Parvulescu[2], Jaroslava Moravkova[1], Radim Pilar[1], Galina Sadovska[1,3], Alena Vondrova[1], Dalibor Kaucky[1], Nikola Kostkova[1,3], Ivan Jirka[1], Somayeh F. Rastegar[1]

[1]*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, CZ-182 23 Prague 8, Czech Republic, [*]Corresponding Author (petr.sazama@jh-inst.cas.cz)*

[2]*University of Bucharest, Department of Organic Chemistry and Catalysis, B-dul Regina Elisabeta 4-12, 030016 Bucharest, Romania*

[3]*University of Pardubice, Studentska 95, 532 10 Pardubice, Czech Republic*

Introduction. The inherent properties of a single atomic carbon layer in graphene offer opportunities for the creation of catalytically active centers tailored on a molecular level on a support with high thermal stability and very high specific surface area (~2600 $m^2 g^{-1}$). The wide range of means of functionalizing the graphene monolayer could be exploited in the development of heterogeneous catalysts with active sites controlled at the atomic level. However, utilization of the unique properties of graphene for application in a catalytic process relies on the development of a three-dimensional (3D) graphene-like catalytic material with connectivity of the pore network, providing good accessibility to the active sites. In this study, metal supported 3D graphene-like microporous carbons synthesized in the beta and faujasite zeolite templates, denoted as β-carbon and Y-carbon, respectively, were analysed with respect to their structure and catalytic properties in comparison with metal supported conventional catalytic materials.

Experimental/methodology. The well-defined and regular 3D channels system of the faujasite zeolite was replicated into the zeolite-templated carbon material by nanocasting. Carbonization of the zeolites was performed using chemical vapour deposition with propylene as a carbon precursor. In the process of zeolite nanocasting, carbon atoms were generated along the walls of the regular zeolite micropores. The subsequent selective removal of the structural lattice of the zeolite provided an ordered 3D microporous graphene-like carbon material [1].

Results and discussion. Structural analyses showed that the β-carbon and Y-carbon are characterized by 3D assembled and highly stable single atomic graphene layers forming an open porous system resembling the regular channel system of the zeolites with a specific surface area comparable to the surface area of graphene (≥2500 $m^2 g^{-1}$) [1]. The curved surface of the 3D graphene-like structure having accessible porosity through the channel system is characterized by the presence of unsaturated carbon atoms at the edges, together with a tunable concentration of oxygen-containing functional (hydroxyl/phenolic and carboxyl) groups. The metal clusters (Pt, Pd, Rh) were introduced into 3D graphene-like carbon materials as active centers for hydrogenation reactions. The relationships between catalytic properties and structural parameters including the effects of the size of metal clusters from a nanometre to a sub-nanometre scale, effects of the interactions of the metal-graphene support and reduced metal–metal coordination were analysed. The materials catalyse the hydrogenation of aromatics, alkenes, alkynes and cycloalkenes into the corresponding alkenes, alkanes and cycloalkanes with exceptionally high reaction rates and selectivity. The study demonstrates the potential of the 3D graphene-like materials for the preparation of metal catalysts with a very high concentration of well dispersed metal clusters of tuneable size.

Zeolite templated 3D graphene-like carbon catalysts represent a novel concept in the field of heterogeneous catalysis, which enables a dramatic increase in the surface area available for active centers and the tuning of catalysts functionality for a wide range of catalytic reactions for hydrogenation/dehydrogenation and processing of hydrocarbons. The results of the study illustrate a method for the exploitation of the unique properties of a single layer of carbon atoms in heterogeneous catalysts characterized by outstanding specific surface area and high thermal stability [1].

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Dry Reforming of Methane for the Syngas Production Catalyzed by Ni-doped Perovskites

Muddasar Safdar[1,2], Nasir Shezad[3], Bogdan Dorneanu[1], Mitra Jafari[1], Sharvendu Shashank Bhat[1], Farid Akhtar[3], Harvey Arellano-García[1]*

[1]*LS- Prozess- und Anlagentechnik, BTU Cottbus- Senftenberg, Cottbus D-03044, Germany*
[2]*Department of Chemical Engineering Technology-GCUF, Faisalabad-38000, Pakistan*
[3]*Department of Engineering Science and Mathematics, Lulea University of Technology, 97187-Luleå, Sweden*

** Corresponding Author's E-mail address: arellano@b-tu.de, muddasar.safdar@b-tu.de*

Abstract

The transformation of greenhouse gases (GHGs) i.e. methane and carbon dioxide into syngas (CO, H_2) via dry reforming of methane (DRM) serves as an excellent sustainable energy solution towards carbon neutrality. The DRM process gained attention to yield the (H_2/CO) syngas ratio as a building block for the production of value-added chemicals and fuels [1]. Therefore, robust and efficient catalysts with high thermal stability and activity are required. The noble metals (Ir, Rh, Ru, Pt, Pd) have been extensively explored as a catalyst owing to excellent conversion rate, stability and turnover frequencies. However, their industrial application is limited due to the high cost. Transition metal-based catalysts are considered a good alternative for the DRM reaction due to their low cost, availability and quick turnover frequencies [2]. Limitations of the Ni-based catalysts are deactivation, accumulation and sintering problems which are detrimental to the conversion efficiency and selectivity for syngas production. Coking is another challenge due to the decomposition of methane ($CH_4 + C \leftrightarrow 2H_2$) and the Boudouard reaction ($2CO \leftrightarrow CO_2 + C$). The aforementioned problems can be overcome using a catalyst with redox properties, and basic sites leading to uniform metal dispersion and resistance against deactivation. One of the possible solutions to address these challenges is the incorporation of active metals into crystalline oxides such as perovskite-type oxides (PTOs) [3]. Perovskite materials having general formula, ABO_3, are used as catalysts precursors or supports. The flexible structure of perovskite materials is capable of accepting a wide range of substitutions with the formation of oxygen vacancies. The higher concentration of oxygen vacancies at the catalyst surface supports the conversion of CO_2 and CH_x species into gaseous products. Moreover, perovskite materials reflect good chemical and mechanical stability under high temperature reaction conditions. Currently, Ni-supported perovskite catalysts are considered useful to improve the activity, stability and carbon deposition-related problems [4].

In view of the above, different perovskite-type supports considering ABO_3 (such as A= Al, La with B=Ce and A=Mg, Mn with B=Zr) were prepared via the sol-gel method. Ni metal loading of 10 wt.% was deposited on prepared perovskite supports via the impregnation method. The catalysts were characterized using XRD and FTIR techniques. The DRM activity was carried out in a tubular reactor as described in our previous study [5]. The catalytic performance was assessed in the temperature range of 500–700 °C, CH_4/CO_2 = 1/1 and under GHSV of 12,000 h^{-1}. Among the prepared catalysts, Ni-doped perovskite combination (i.e. A=Mg with B=Zr)$O_{3-\delta}$ exhibited higher (CH_4, CO_2) conversion ca. (69, 59) percent and syngas yield of ca. (H_2/CO =0.72) at 700 °C. This indicates that the magnesium zirconate perovskite catalyst established strong interfacial metal-support interaction, redox properties and surface basic sites that linked with good performance of the catalyst during DRM process.

Keywords: Dry reforming of methane (DRM), Ni-Perovskites, Syngas production, Greenhouse gases (GHGs)

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Lanthanide-based iron perovskites for catalytic rWGS

S. Saini[1], A. Martinez Martin[2], D. Neagu[3], W. Hu[2], I. S. Metcalfe[2], K. Kousi[1,*]

[1] *University of Surrey, GU2 7XH, Guilford, United Kingdom*
[2] *Newcastle University, NE1 7RU, Newcastle upon Tyne, United Kingdom*
[3] *University of Strathclyde, G1 1XQ, Glasgow, United Kingdom*

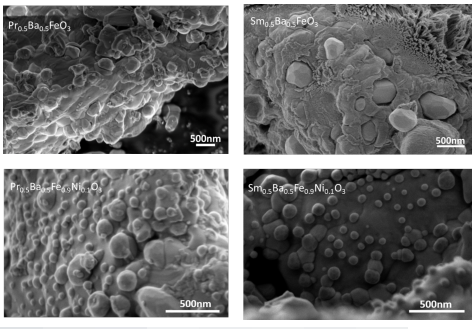
[*]k.kousi@surrey.ac.uk

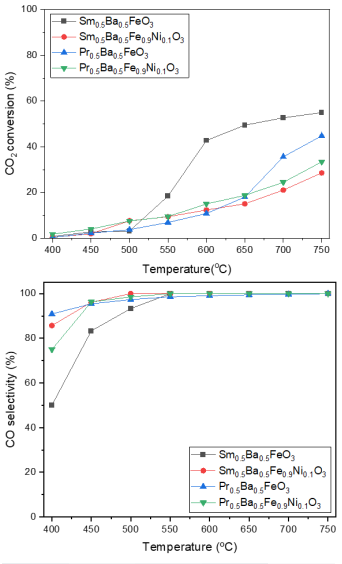
Keywords: perovskites, exsolution, lanthanide, reverse water-gas shift

Introduction: CO is a precursor of utmost importance in many chemical processes. In this context of decarbonisation and reutilisation of industrial by-products, such as CO_2, reverse water-gas shift (rWGS) reaction, where CO and H_2O are generated, has gained attention. rWGS processes require high temperatures and the presence of catalysts that possess high selectivity towards CO as well as tolerance to high temperatures and agglomeration. Perovskites (ABO_3) with rare-earth elements (or lanthanides) in the A-site are well-known to be stable at high temperatures in catalytic processes whilst able to form oxygen vacancies hence improving CO_2 activation. Fe and Ni in the B-site are known to activate the rWGS reaction[1]. These perovskites can be decomposed into composites (exsolution process). Exsolution of metallic nanoparticles has proven to improve reactivity and their resistance towards coking formation and sintering[2]. Here we study and compare the effects of using different rare-earth elements in the A-site in a $Ln_{0.5}Ba_{0.5}Fe_{1-x}Ni_xO_3$ perovskite (Ln = Pr, Sm; x = 0, 0.1) as well as how the conversion towards desired products can be enhanced by the addition of a dopant when implemented in the rWGS reaction.

Materials and Methods: High purity precursors were used to prepare the $Ln_{0.5}Ba_{0.5}Fe_{1-x}Ni_xO_3$ catalysts by modified solid state method. Exsolution of particles was achieved by reducing the single-phase perovskites under 5% H_2 at 900 ºC for 10h. Purity and crystallinity study was done by Powder X-Ray Diffraction (XRD) and Rietveld refinement was carried out using TOPAS academic v7. Micro and nanostructure, morphology, atomic distribution were studied by scanning electron microscopy (SEM). Specific surface area was studied by N_2 adsorption, with the Brunauer-Emmett-Teller method (BET). rWGS catalytic tests were conducted in a continuous fixed bed quartz reactor, using 1 mmol of catalyst and CO_2:H_2 in a 1:2 ratio, 50 mL/min of reactant gases.

Results and discussion: Single-phase perovskites were synthesised and characterised by XRD and further by Rietveld refinement to confirm the high purity of the samples, SEM and BET. After exsolution Fe particles were observed for the non-doped perovskites (x = 0) and Fe-Ni alloys were confirmed for the Ni-doped perovskites (x = 0.1), shown in Figure 1. $Sm_{0.5}Ba_{0.5}FeO_3$ shows remarkably higher conversion (Figure 2) than the rest of catalysts, given its larger number of oxygen vacancies within its structure, hence activating CO_2. However, although more active, its selectivity towards CO is not as high as it is for Ni-doped samples. Ni-doped samples, despite not being as active as the latter, display a remarkably high selectivity towards CO, even at lower temperatures.





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$Ti_{1-y}W_yO_2N_x$ Photo-Oxidation Catalysts: From Synthesis to VOC Degradation

Sofia Salli, Kristina Maliutina and Emma Richards*

**School of Chemistry, Cardiff University, Main Building, Cardiff, UK, CF10 3AT*

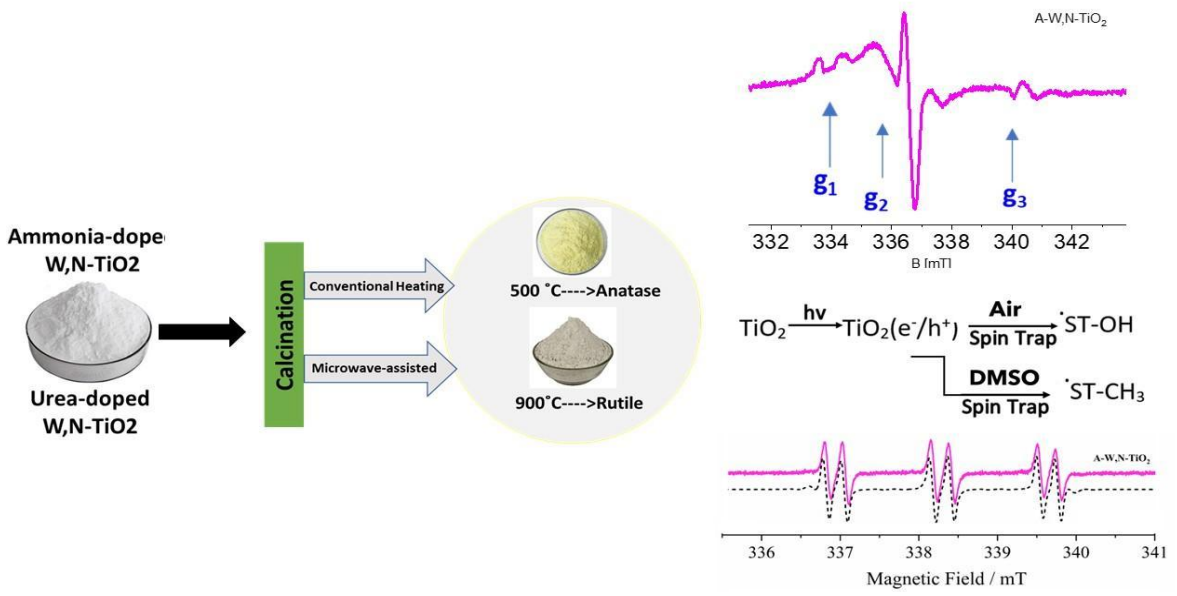
Keywords: EPR spectroscopy, photocatalysis, materials characterisation, pollutants

Introduction: We report novel semiconducting nanoarchitectures based on earth-rich elements, with the general formula $Ti_{1-y}W_yO_2N_x$ as potential heterogeneous catalysts for VOC degradation and organic transformations. During irradiation of semiconducting materials, such as TiO_2, with energy exceeding their bandgap, electron and hole charge carriers (e^-/h^+) are produced. Subsequent migration of these charge carriers to the surface facilitates generation of Reactive Oxygen Species which exhibit superior oxidising power that promotes the degradation of organic compounds, such as toluene and formaldehyde.[1] The redox potential of the material and the performance upon visible light irradiation can be modified by introducing heteroatom dopants.[2]

Experimental/methodology: In our comparative study, we employ different nitrogen precursors (namely ammonia and urea) and calcination strategies, including microwave-assisted and furnace heating, to generate a series of $Ti_{1-y}W_yO_2N_x$ materials via sol-gel synthesis. Pure-phase anatase and rutile -TiO_2 polymorphs were prepared and fully characterised (BET, XPS, XRD, UV-Vis, SEM, Raman, FTIR).

Results and discussion: The introduction of intra-band gap states from both W-based acceptor levels, and N-based donor levels, the energy gap of the dopant material was lowered and thus improves alignment with incident solar radiation wavelengths.

To further explore the mechanism of photoactivity, we use Electron Paramagnetic Resonance (EPR) spectroscopy to characterise the transient charge-carriers and reactive radical species. The redox changes of the dopant defect sites formed in these materials are investigated upon in-situ irradiation, and the role of ˙OH/ ˙OOH radicals in the decomposition of dimethyl sulfoxide is determined.



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Kinetic Study of seed-assisted crystallization of CON-type zeolite

M. Sawada[1], H. Onozuka[2], S. Tsutsuminal[2], J. N. Kondo[1] and T. Yokoi[1*]

[1]*Tokyo Institute of Technology, Yokohama, Japan*
[2]*Mitsubishi Chemical Corporation, Yokohama, Japan*
[*] *yokoi@cat.res.titech.ac.jp*

Keywords: Zeolite, Boroaluminosilicate, Crystallization

Introduction. Recently, the zeolites with 10- and 12-ring pores have been paid attention in terms of their potential long catalytic lifetimes and high propylene selectivity compared to those with 8-ring systems[1]. We have first found that the CON-type boroaluminosilicate zeolite was an excellent catalyst for the selective formation of light olefins in the methanol to olefins (MTO) reaction[2,3]. It has been well known that in zeolite synthesis, the seed crystal affects the particle size as well as crystallization process. However, the impact of the seed crystal on the crystallization of the CON-type zeolite has not fully been investigated[4]. Originally, Beta zeolite has been used as seed crystals for crystallizing the CON structure. In this study, we synthesized the CON-type zeolites with either CIT-1 ([Al,B]-CIT-1_CIT-1) or beta ([Al,B]-CIT-1_Beta) as seed crystals, and clarified the influence of the seed crystals on the crystallization of the CON-type zeolite and their physicochemical and catalytic properties.

Experimental/methodology. The CON-type zeolites [Al,B]-CON were hydrothermally synthesized from the aqueous gel, containing a N,N,N-Trimethyl-(–)-cis-myrtanylammonium hydroxide (organic structure-directing agent), NaOH, boric acid, aluminum sulfate, fumed silica and 2 wt % of CIT-1, CON-type zeolite (Si/Al =20, 270) or zeolite beta (Si/Al = 12) as seed crystals. The prepared gel was crystallized at 170 °C for 7 days. The obtained samples were characterized by XRD, SEM, ICP-AES, N_2 adsorption, NH_3-TPD analysis.

Result and discussion. By the XRD patterns, the CON-type structure was crystallized regardless of the type of the seed after the hydrothermal treatment for 7 days. The SEM images showed that [Al,B]-CIT-1_CIT-1 and [Al,B]-CIT-1_Beta have almost similar particle morphology. The crystallization processes for both samples were monitored by the XRD patterns (Figure 1). There was a significant difference in the crystallization rate between CIT-1 and beta as seed crystals; the use of CIT-1 zeolite as seed crystals lead to the formation of the CON framework after 84 h, while that of beta required 108 h for the crystallization, indicating that the use of the seed crystals with targeted structure enables a faster crystallization. Note that, in the absence the seed crystals, the crystallization was unsuccessful even after 7 days. When beta zeolite is used as seed crystals, beta must be dissolved once, forming oligomers such as composite building unit (CBU), and then nucleation would start. On the other hand, the use of CIT-1 as seed crystals, the crystal growth would be initiated from the surface of the seed crystal, leading to the fast crystallization.

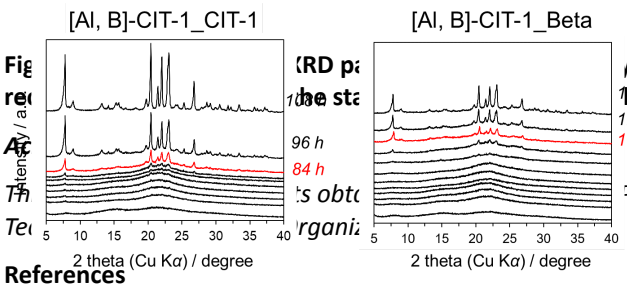

Fig **XRD pa** **ydrothermal treatment: the diffraction pattern was re** **he sta** **hesis in [Al, B]-CIT-1_CIT-1 and [Al, B]-CIT-1_Beta.**

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Structured catalysts for electrified magnetic catalysis

A. Sedminek[1,2*], D. Makovec[1], A. Kocjan[3], J. Teržan[1,4], B. Likozar[4], V. Middelkoop[5], F. Sotoodeh[6], S. Gyergyek[1]

[1] *Department for Material Synthesis, Jožef Stefan Institute, Slovenia*
[2] *Faculty of Chemistry and Chemical Engineering, University of Maribor, Slovenia*
[3] *Department for Nanostructured Materials, Jožef Stefan Institute, Slovenia*
[4] *Department for Catalysis in Chemical Reaction Engineering, National Institute of Chemistry, Slovenia*
[5] *Sustainable Materials Management, VITO NV, Belgium*
[6] *C2CAT B.V., Netherlands*
anja.sedminek@ijs.si

Keywords: magnetic, electrification, ruthenium, cobalt, nickel, structured catalyst.

Introduction. Magnetic heating of the catalyst bed has several advantages, such as rapid heating, allowing on-demand ignition and hasty achievement of stationary conditions. With this, the catalytic reaction is limited only by kinetics and not heat transfer limitations [1]. In our work, we developed structured nanocomposite catalysts for electrified magnetic catalysis, such as ammonia synthesis/decomposition, hydrogenation/dehydrogenation of LOHC etc. Those consist of CoNi nanoparticles (NPs) embedded within the alumina matrix [2] decorated with catalytic Ru NPs.

Experimental/methodology. Three different methodologies were used to prepare structured nanocomposite catalysts: i. The CoNi-A-Ru-I catalyst was prepared in a three-step process. In the first step, the CoNi mixed hydroxide-containing boehmite powder was synthesized by aqueous co-precipitation of Co and Ni cations followed by AlN hydrolysis [3, 4]. In the second step, the powder was arranged into a structured catalyst. After thermal treatment, Ru was deposited by impregnation in the last step. ii. The CoNi-A-Ru-P catalyst was also prepared by a three-step process. The first step is the same as described above. After thermal treatment (900 °C, 1 h, H_2 atmosphere), Ru was deposited by precipitation in the second step. And in the last step, the powder arranged into a structured catalyst. iii. For the synthesis of the A-CoNiRu catalyst in the first step, alumina powder was prepared by hydrolysis of AlN in the presence of colloidal silica, followed by thermal treatment (500 °C, 1 h, stagnant air). Then the powder was arranged into a structured catalyst. In the last step, catalytic and magnetic NPs were deposited on the catalyst. The catalysts were extensively characterized and tested for magnetic catalysis in a custom-made high-pressure reactor. As the AC power source, a high-frequency generator was used, to which a copper tube coil is attached. The reaction yield was determined by on-line gas chromatography and mass spectrometry.

Results and discussion. The H_2-TPR profile of CoNi mixed hydroxide-containing boehmite shows distinct temperature clusters at low (~300 °C) and high (~850 °C) temperatures, indicating a two-step reduction process. Structural analysis shows that heat treatment in H_2 atmosphere at 900 °C reduces the CoNi mixed hydroxides to a metallic CoNi alloy, while boehmite dehydrates to metastable γ-Al_2O_3. The size of the CoNi NPs ranges from 10 to 18 nm. Measurements of the temperature-dependent magnetic properties in H_2 atmosphere revealed that CoNi NPs exhibit high (> 940 °C) Curie temperature and soft magnetic properties, indicating their high potential for magnetic heating. Our best nanocomposite powder reached temperatures above 500 °C in less than a minute under magnetic heating while it cooled to ambient temperature in a few minutes when the field was shut down. The physical and chemical properties of the prepared structured catalysts will be presented.

Acknowledgments

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P-modified Pd catalysts for hydrogenation of aromatic compounds for chemical hydrogen storage

A. Seitz, I. Backes, P. Schühle*

Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany
**patrick.schuehle@fau.de*

Theoretical background

Renewable hydrogen is a promising energy carrier to decarbonise industrial, energy and mobility applications. Hydrogen can be stored and transported in liquid organic hydrogen carrier (LOHC) systems, allowing safe and loss-free H_2-handling and the use of the existing liquid fuel infrastructure [1]. H_2-storage is performed in an exothermic catalytic hydrogenation reaction of the used LOHC [1]. The endothermic dehydrogenation releases pure hydrogen that can be used at time and place of a H_2-demand [1].

Palladium based catalysts have been shown to possess high productivity in the hydrogenation of the LOHC system dibenzyltoluene/perhydro-dibenzyltoluene [2]. The same study also found that the Pd/Al_2O_3 catalyst still exhibits adequate activity when the used H_2 is contamined with CO [2]. To improve the efficiency of LOHC hydrogenation using hydrogen from different renewable and recycled sources, the productivity and CO-stability of Pd catalysts must be further optimised.

Phosphorous-modification has previously shown to positively effect transition metal catalyst performances. For instance P-doped Pd/Al_2O_3 showed increased activity and stability in anthraquinone hydrogenation [3]. This was attributed to an improved thermal stability, increased Pd dispersion and enhanced interaction between Pd and support, decreasing Pd-loss during the reaction [3]. Additionally, CO-TPD analysis by Chandler et al. showed that P-modification of transition metal catalysts weakens the binding strength between CO and metal and therefore increases CO-stability [4].

Inspired by this promising approach we herein pursue P-modification of Pd catalysts to improve LOHC hydrogenation with pure and impure hydrogen.

Experimental procedure

P-modification of a commercial Pd/Al_2O_3 powder catalyst with 5 wt.-% Pd is conducted by wet-impregnation with phosphorous acid at different molar P/Pd ratios. This is done in aqueous solution which is stirred at room temperature for 16 h. After solvent evaporation at 80 °C and 50 mbar the catalyst is reduced at different temperatures under diluted hydrogen for 2 h.

The prepared catalysts are tested in the hydrogenation of the LOHC system benzyltoluene (BT)/perhydro-benzyltoluene. Batch experiments are carried out at 200 – 250 °C, 30 bar H_2-pressure and 0.05 mol-% Pd. Liquid samples are drawn regularly and are analysed via GC-FID to determine the degree of hydrogenation (DoH) of BT, which is a measure of the hydrogen loading of the LOHC. The hydrogenation productivity *P* of the catalyst is calculated in the DoH-range of 30 to 50 %.

Results

Our results show that P-modification of Pd/Al_2O_3 catalysts can increase the productivity of the commercial catalyst by up to 60 % under pure hydrogen conditions. The variation of the molar P/Pd ratio suggests an ideal ratio of 2.0. Formation of by-products was not increased by P-modification despite the higher activity of these catalysts. Detailed results of the hydrogenation experiments, further material analysis and hydrogenation using impure hydrogen will be shown on the poster.

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Effect of the B cation in a perovskite as precursor for the catalytic m-cresol hydrodeoxygenation reaction.

T. Fonseca[1], C. Herrera[1,2], C. Sepúlveda[1,2], G. Pecchi[1,2*]

[1]*Depto Físico-Química, Fac Cs Químicas, Universidad de Concepción, Chile*
[2] *Millennium Nuclei on Catalytic Process towards Sustainable Chemistry (CSC), Chile*
[*]*gpecchi@udec.cl*

Keywords: m-cresol, perovskites, hydrogenation, cation B

Introduction. The importance of the lignocellulosic biomass valorization is constantly increasing due to its abundant availability in nature, low cost and it is a renewable carbon source, unlike petroleum derivatives. From the pyrolysis of the lignin of the biomass, 30 wt.% of phenolic compounds such as cresols, guaiacols, syringols and phenols can be obtained[1], which can be subjected to catalytic hydrotreatment (HDO) to improve their properties and obtain high added-value chemicals[2]. Recently, promising results have been found in HDO reactions using perovskite type structure [3]. In this work the catalytic evaluation of three pure (ABO_3) perovskite $LaCoO_3$, $LaNiO_3$, $LaFeO_3$ and three substituted ($AB_{0.5}B'_{0.5}O_3$) $LaFe_{0,5}Co_{0,5}O_3$, $LaFe_{0,5}Ni_{0,5}O_3$ and $LaCo_{0,5}Ni_{0,5}O_3$ previosuly reduced and passivated at 500°C perovskites in the HDO of m-cresol is reported.

Experimental/methodology. The pure and substituted perovskites were synthesized using the citrate method and characterized by X-Ray diffraction (XRD), N_2 physisorption at 77 K, thermal programmed reduction (TPR H_2) and thermal programmed desorption of CO_2 (TPD CO_2).The catalytic activity was evaluated in a semi-batch reactor in the m-cresol HDO reaction at 200°C and 50 bar of H_2 using the previously reduced catalysts.

Results and discussion.

The characterization results show that after reduction the $LaFeO_3$, $LaFe_{0.5}Co_{0.5}O_3$ and $LaFe_{0.5}Ni_{0.5}O_3$ perovskites did not show reduction of the structure, while the formation of metallic Co and Ni was found in the $LaCoO_3$, $LaNiO_3$ and $LaCo_{0.5}Ni_{0.5}O_3$ perovskites. With regard to the basic properties, in the reduced and passivated perovskites only the $LaCoO_3$, $LaNiO_3$ and $LaCo_{0.5}Ni_{0.5}O_3$ show basic sites formation. The $LaFeO_3$, $LaFe_{0,5}Ni_{0,5}O_3$ and $LaFe_{0,5}Co_{0,5}O_3$ did not present activity while the more active perovskite was $LaCo_{0,5}Ni_{0,5}O_3$ (Table) atributed to presence of Co and Ni metallic species which are active in the m-cresol conversion. The principal product detected on the active perovskites, with no Fe content in the B or B´cation was 3-methylcyclohexanol (3-MCXol) indicating that over these catalysts the reaction occurs by direct hydrogenation of the aromatic ring to 3-methyl-2-cyclohexenol (no detected) which is full hydrogenated to (3-MCXol). By tautomerization, 3-MCXol is converted in low amount to 3-methylcicloxenanone (3-MCXone), which is asocciated to the presence of basic sites. This route have been reported prevously, were is proposed that hydrogenation mechanism is atributed to presence of less oxophilic catalysts [4,5]

Perovskite	Initial rate r_0*10^4 (mol/g*s)	Distribution of products at 40 % of m-cresol conversion				
		3-MCXol	3-MCXone	Others	Phenol	Toluene
$LaCoO_3$	18.9	85.4	4.2	8.1	3.2	2.0
$LaNiO_3$	4.4	82.5	13.5	11.7	3.4	1.4
$LaCo_{0,5}Ni_{0,5}O_3$	26.5	85.4	4.3	8.1	3.2	2.0

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Au-TiO_2 catalysts for plasmon-driven photocatalytic wastewater treatment: Synthesis and characterization

Estrella Serra-Pérez, Gregor Žerjav, Sebastijan Kovačič, Nataša Novak Tušar, Albin Pintar*

Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia
albin.pintar@ki.si

Keywords: heterogeneous photocatalysis, plasmonic catalysts, titanium nanorods, wastewater treatment

Introduction.
TiO_2 is one of the most studied catalysts for heterogeneous photocatalytic oxidation of organic pollutants dissolved in wastewaters, due to its strong oxidizing power, non-toxicity, long-term photostability, chemical stability, low cost, and insolubility in water. However, its inability to absorb light in the visible-light range severely limits its practical application. One way to overcome this disadvantage of TiO_2 is to combine it with noble metals (Au, Ag, Pt, etc.). The plasmonic properties of noble metals allow TiO_2 to have catalytic activity in the visible-light region. Therefore, there is a great interest in further research of TiO_2-based catalysts doped with noble metals to promote heterogeneous photocatalytic oxidation of organic pollutants in wastewaters under visible-light illumination [1,2]. The purpose of this work is to systematically investigate an influence of morphological and surface properties on performance of Au-TiO_2 catalysts in the process of visible-light trigerred photocatalytic oxidation of water-dissolved organic pollutants.

Experimental/methodology.
In this study, Au-TiO_2 catalysts were prepared using different TiO_2 supports. First, different TiO_2 nanorods (TNRs) were synthesized by alkaline hydrothermal synthesis, differing in their surface and structural properties. Once the TNRs were obtained, wet impregnation followed using an aqueous solution of $HAuCl_4 \cdot 3H_2O$ to infiltrate the TNRs with gold nanoparticles. Finally, calcination at 300 °C resulted in TiO_2 TNRs doped with elemental Au. Au-TiO_2 catalysts were further characterized using X-ray diffraction, SEM, N_2 physisorption, UV-VIS diffuse-reflectance (DR) spectroscopy, zeta potential, and solid-state photoluminescence (PL) techniques.

Results and discussion.
Different synthesis conditions allowed us to obtain TNRs with zeta potential between 3.9 and 5.9, and specific surface area (S_{BET}) between 87 and 111 m^2/g. The thermal stability of all the TNRs thus obtained was unchanged up to 300 °C, so calcination was performed at this temperature to obtain Au in the desired oxidation state. UV-VIS DR spectra show an additional absorption peak at approx. 550 nm, attributed to the presence of localized surface plasmon resonance (LSPR) effect, while solid-state PL spectra show the influence of the Schottky barrier at the TiO_2 support/Au ensemble junction on the rate of recombination of charge carriers. Both analyses confirmed the VIS activity of synthesized Au-TiO_2 catalysts. Several tests were performed with scavengers, such as ABTS and DPPH to investigate the production of “hot electrons” and reactive oxygen species. In addition, the photocatalytic activity of examined solids was evaluated using coumarin as a fluorescence probe molecule to selectively determine their ability regarding the formation of hydroxyl radicals. Catalytic tests with water-dissolved model organic pollutants (such as bisphenol A) and characterization using XPS and TEM analyses are in progress.

Acknowledgements
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Rationally designed bifunctional catalyst with metal incorporated core-shell silicalite-1 architecture

Urvashi Sharma[1†], Manjesh Kumar[1‡]

[1]*Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi, India*
‡*manjeshkumar@chemical.iitd.ac.in,* †*urvashi.sharma@chemical.iitd.ac.in*

Keywords: Metal nanoparticle and cluster, core-shell zeolite, bifunctional catalyst

Introduction. A promising category of catalysts for a wide range of organic reactions and gas separation applications is represented by zeolitic frameworks loaded with diverse metal sites [1]. However, there are significant challenges to address, including diffusion limitations, catalyst lifetime, instability under harsh reaction conditions, and poisoning due to byproducts [2]. In this study, we present viable and environmentally friendly synthetic methods to create a bifunctional catalyst. This catalyst exhibits controlled topological distribution of metal sites and a core-shell architecture, effectively overcoming diffusion limitations. Our research offers valuable insights into the design of bifunctional catalysts with desired physicochemical properties, providing enhanced lifetime and activity.

Experimental/methodology. To obtain silicalite-1 crystals, a silica source combined with an alkaline structure directing agent (SDA) was stirred at room temperature, resulting in the formation of a viscous gel. The gel was then subjected to hydrothermal treatment within the temperature range of 100 to 200°C for a duration of 24 to 96 hours. This process yielded the desired silicalite-1 crystals. Subsequently, the obtained product underwent thermal treatment in an aqueous alkaline solution to achieve hollow zeolite crystals. To incorporate metal clusters and nanoparticles into the core-shell structure of silicalite-1, the metal complex was reacted with silicalite-1, enabling the integration of the metal clusters within the core-shell zeolite.

Results and discussion. Treatment of silicalite-1 with alkaline solution results in the formation of core-shell crystals, where the thickness of the shell ranges from 10 to 100 nm. For enhanced catalysis and stability, synthesizing core-shell zeolite crystals is highly desirable. We explored the new synthetic protocols here for obtaining silicalite-1 hollow crystals incorporated with metal clusters of Pd and Ag. Here, figure 1 (A), (C) and (F) show the hollow zeolite crystals with metal nanoparticles of size 2 to 10 nm inside the hollow domain. Whereas, figure (B), (D) and (E) shows that the small nanoparticles of the metal are dispersed on the surface of zeolite crystal. Similar trends are observed in the both the metals. We carried out numerous synthetic protocols to generate the zeolite crystals with controlled topological distribution of metal sites. The mechanistic studies and the detailed analysis results will be presented at the conference.

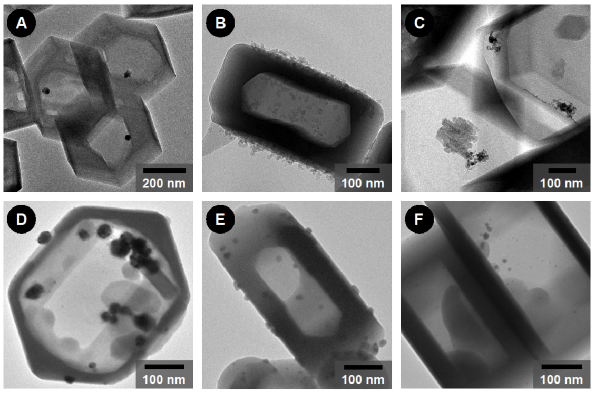

Figure 1: TEM images of the samples (A) Pd loaded silicalite-1 synthesized using a single step route, (B) Pd loaded silicalite-1 synthesized using a two-step route, (C) Pd loaded silicalite-1 synthesized using in- situ process, (D) Ag loaded silicalite-1 synthesized using a single step route, (E) Ag loaded silicalite-1 synthesized using a two-step route, (F) Ag loaded silicalite-1 synthesized using in-situ process.

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Gas-phase Pd and PdZn clusters deposited on ZnO and SiO_2 as model catalyst for CO_2 hydrogenation to methanol

Imran Abbas[1*], Sumant Phadke[2,3], Joao Coroa[1,4], Jinlong Yin[4], Olga Safonova[2,3], Christophe Coperet[3], Didier Grandjean[1], Ewald Janssens[1]

[1]*Quantum Solid-State Physics, KU Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium*
[2]*Paul Scherrer Institute, Villigen PSI, 5232, Switzerland*
[3]*Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zurich, Switzerland*
[4]*Teer Coatings Ltd., West Stone House, West Stone, Berry Hill Industrial Estate, Droitwich, WR9 9AS, UK*
[*]*imran.abbas@kuleuven.be*

Keywords: CO_2 hydrogenation, methanol synthesis, metal-support interface, heterogeneous catalysis, gas-phase clusters

Introduction. Supported Pd nanoparticles have demonstrated promising catalytic activity for the hydrogenation of CO_2 into methanol but the nature of the metal-support interface and its role in the reaction mechanism remains a topic of ongoing research [1-3]. We have produced model catalysts by depositing well-defined Pd and PdZn clusters directly onto ZnO and SiO_2 powders using the Cluster Beam Deposition (CBD) technology. Well defined Pd and PdZn catalysts will facilitate the investigation of the Pd-Zn and Pd-ZnO interface to unravel their structure-activity relationship.

Experimental/methodology. Pd and PdZn clusters of different compositions were produced in high vacuum using a magnetron sputtering-based CBD at Teer Coatings Limited, UK and deposited onto one gram of each pre-dried oxide powder placed in a vibrating cup for uniform deposition of size-controlled clusters containing 500 to 700 atoms. 0.1 wt% Pd clusters loading on oxide powders was confirmed using ICP-OES and the size of clusters deposited on TEM grid was found to be 3-4nm (figure 1). The samples were activated *in situ* in pure hydrogen at 120°C for 30 minutes before catalytic tests. Catalytic activity tests for CO_2 hydrogenation were performed at 210°C and 40 bar on 0.4 g of each sample loaded in a plug flow reactor in a 5 mL/min feed gas of $3H_2$:$1CO_2$.

Results and discussion. A very small concentration of Pd clusters (0.1wt%) on ZnO is found to promote the CO_2 hydrogenation to methanol and CO while only a very small activity is observed for Pd/SiO_2. A four-time increase of the CO_2 hydrogenation rate compared to sum of blank ZnO and Pd/SiO_2 is reported in Figure 1, confirming the excellent Pd-ZnO synergy in these model catalysts.

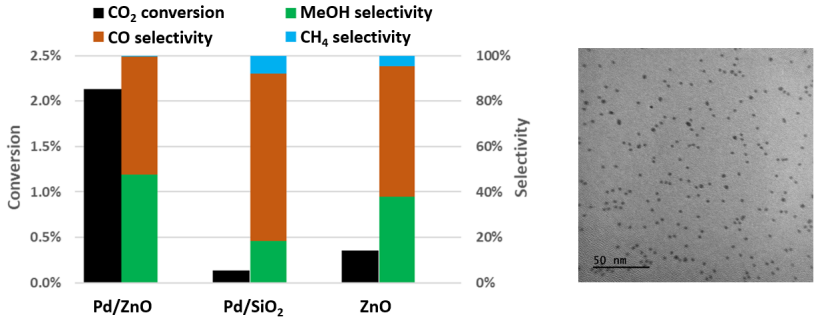

Figure 1: (left)CO_2 conversion and product selectivity at 210°C ; (right) Image of Pd_{604} clusters on a TEM grid.

To investigate further the Pd-ZnO synergy and uncover structure-activity relationship, detailed structural investigation of Pd clusters on ZnO and PdZn clusters on SiO_2 under CO_2 hydrogenation conditions will be performed using in situ X-ray absorption spectroscopy and correlated to the catalytic activity.

Acknowledgments.
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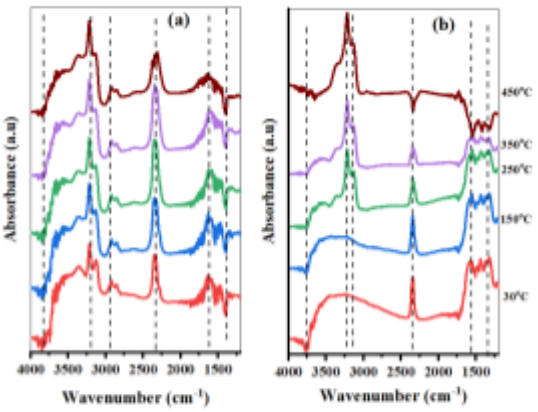
Non-oxidative Propane Dehydrogenation using Precious Metal-Free Chloride-Treated Metal Oxides

G. Celik[1*] and A. Bouziani[1]
[1]*Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey*
[*]*gcelik@metu.edu.tr*

Introduction. Propylene production from nonoxidative dehydrogenation of propane (NPDH) is a well-recognized process. Yet, some downsides including toxicity of chromium and high-priced and low abundance platinum still need to be overcome. Metal oxides such as TiO_2-based or ZrO_2-based catalysts are promising alternatives having distinct bulk defects. For ZrO_2 based metal oxides, the literature has established that two neighboring coordinatively unsaturated Zr cations (Zr_{cus}) situated at the oxygen vacancies (OVs) are the active sites responsible for activating the C-H bonds of propane[1]. Regarding TiO_2, It was reported that the fourfold-coordinated Ti atoms surrounding oxygen vacancies (OVs) are the main active sites for PDH[2]. Hence, the OVs and defects are vital for the high activity of these metal oxides. Herein, we propose a chloride treated ZrO_2 (Cl-ZrO_2) ZrO_2 and (Cl-TiO_2) catalysts for the nonoxidative alkane dehydrogenation. Theoretically, the incorporation of anion into an oxide will lead to an increase in the surface basicity[3] and anions situated at the site of oxygen may generate more lattice defects, enhancing the activity of gaseous reactants and repressing deep dehydrogenation[4].

Experimental/methodology. Metal oxides were synthesized via sol-gel technique. HCl (1M, 4mL) was used as the Cl^- source. The obtained catalysts were characterized by X-Ray Diffraction (XRD), laser Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), N_2-physisorption, desorption of propene with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and DRIFTS of adsorbed CO_2. Finally, the Cl-ZrO_2 was tested for propane and n-butane nonoxidative dehydrogenation at 550°C.

Results and discussion. The characterization results showed that the chloride treatment resulted in changes of crystal phase, surface area, acidity and basicity. After the treatment, the ZrO_2-based catalysts had chloride doped into the structure and no detectable change in number of OVs, whereas TiO_2-based catalysts no chloride was found in the TiO_2 based catalysts. Interestingly, chloride treatment did not cause chloride doping, but increased the number and nature of oxygen vacancies. The type of OVs created by chloride treatment over TiO_2 was shown to be different and more active than the ones created by in-situ reduction under H_2, as evidenced by EPR and Temperature Programmed Reduction of CO, respectively. Furthermore, the DRIFT spectra taken after C_3H_6 adsorption displayed a weaker interaction of propylene with the catalyst surface after chlorine addition (Figure 1). Hence the desorption of propylene from Cl-ZrO_2 seen in TPD experiments was easier and may prevent undesired deep-dehydrogenation. The chloride treated catalysts improved the catalytic activity (more than three times per site) and improved the selectivity to ~99%. In conclusion, the results showed that chloride treatment of metal oxides during synthesis allowed us to tune important catalyst attributes such as basicity and desorption tendency of propylene, consequently altering its catalytic activity and preventing deep dehydrogenation in the nonoxidative dehydrogenation of alkane.



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Iron-based catalyst for production of hydrogen and CNTs through the catalytic decomposition of methane

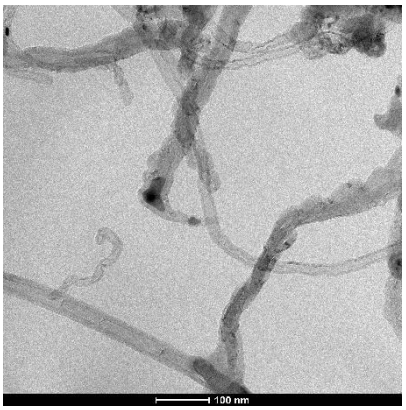
S. Shekhar[1], K.K. Pant[1*], S. Roy[1], R. Joshi[2]
1.Department of Chemical Engineering, Indian Institute of Technology, Delhi, India
2.School of Materials Science & Engineering, University of New South Wales, Sydney, Australia
kkpant@chemical.iitd.ac.in

Keywords: Hydrogen, Catalytic decomposition of Methane (CDM), CNTs

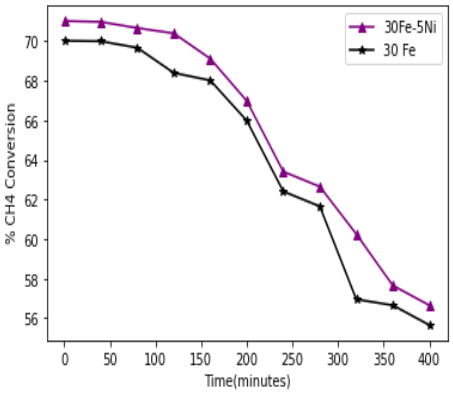
Introduction. The promising technique of catalytic decomposition of methane (CDM) aims to produce hydrogen and valuable byproduct like CNTs without releasing greenhouse gas emissions [1]. However, a significant challenge in making this process commercially viable is the development of an appropriate catalyst that can maintain long-term stability, exhibit strong catalytic activity and be cost-effective. Nickel is the best catalyst for this process [2], but due to the rapid decomposition of nickel it is not suitable for the long run. Since iron-based catalysts performance is comparable with Ni catalysts because, Fe catalysts can survive temperatures of 700 °C and above, it is possible to achieve larger methane conversions with them than with Ni catalysts, leading to a favorable shift in the equilibrium. On the other side, greater temperatures hasten the catalyst's deactivation [3].

Experiment /methodology. Using incipient technique, monometallic and bimetallic catalysts were made, containing 30 wt% metal of Fe, 25Fe:5Ni. The calculated quantity of spherical Alumina (100–150 mesh) was dissolved in the metal salt solution that had already been prepared. Before the water was removed by rotary vacuum evaporation, the produced slurry was constantly agitated for two hours. The slurry was then put in the oven to dry for an entire night at 120°C. The resulting cake was then calcined in the furnace for 5 hours at a ramp rate of 3 °C/min from ambient temperature to 750 °C. Before each reaction, the catalyst was reduced in-situ using hydrogen and nitrogen gas (1:1 by volume) at a total flow of 40 mL/min at NTP.

Results and discussion. The experimental findings of methane conversion are shown in fig. The reaction was conducted at 800°C and an atmospheric pressure while the feed was kept at 4,000 mL h^{-1} g^{-1} cat. space velocity.



TEM Image of CNT



Conversion of methane

The figure illustrates that the addition of nickel (Ni) resulted in a slight increase in the conversion rate. However, the significant finding from the Raman spectroscopic is the quality of carbon nanotubes (CNTs) produced. It is evident that increasing the nickel content enhances the quality of CNTs, as the I_G/I_D ratio is improved.

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The Effect of Vanadium Substitution into Cobalt Oxide Catalysts for Selective 2-Propanol Oxidation

Hauke Scheele[1], Nicolas Cosanne[1], Sharif Najafishirtari[1], Malte Behrens[1*]
[1]*Christian-Albrechts-Universität zu Kiel, 24118 Kiel*
[*]*mbehrens@ac.uni-kiel.de*

Keywords: 2-Propanol oxidation, Spinel Oxide, Cobalt, Vanadium

Introduction. Selective oxidation of 2-propanol to acetone is a probe reaction for redox and acid-base properties[1] and cobalt oxide with spinel structure showed high catalytic activity.[1] During the heating phase of a transient test, a first maximum of 2-propanol consumption rate was observed, i.e. a low-temperature channel, and attributed to Co^{3+}.[1] This maximum is not present during cooling due to poisoning by carbonaceous species like acetates and reduction of Co^{3+} to Co^{2+}.[1,2] In this work, we studied the effects of partial substitution of the catalytic active Co^{3+} ions by V^{3+} on the catalytic behavior.

Experimental/methodology. The precursors were synthesized through the hydrothermal method and subsequently thermally decomposed to the spinel oxides in a muffle furnace at 400 °C under air atmosphere. 2-Propanol oxidation was carried out on the catalysts (100 mg, 250-355 µm) in a home-build setup with 0.18 % 2-propanol + 0.18 % O_2 balanced in nitrogen as dry feed gas or with the addition of 2 % water as wet feed after an oxidative pretreatment (TPO @ 300 °C) between the dry and wet runs.

Results and discussion. Needle-shaped cobalt hydroxycarbonate precursors $Co_6(CO_3)_2(OH)_8 \cdot H_2O$ were synthesized and calcined to the spinels with various V contents. EDX mapping shows a homogeneous distribution of Co, V and O, but with increasing V content, a crystalline $Co_3V_2O_8$ by-phase was obtained. Calculated from Pawley Fits, the spinel lattice parameter increases with V content, indicating the incorporation of V into the spinel structure. Within the selective catalytic oxidation of 2-propanol, the pure Co_3O_4 spinel shows the typical behavior as reported in the literature.[1] If V is present, the increase of the 2-propanol consumption rate changes significantly (Figure 1 a & d). During heating, there is a sigmoidal increase directly to the maximum without a distinct low-temperature path. Contrary to Co_3O_4, the acetone formation does not follow the 2-propanol consumption trend (Figure 1 b & e) but shows a maximum at around 200 °C. The acetone formation peak reappears during cooling, which is, however, shifted to higher temperatures. Above temperatures of 150 °C, propene is formed in significant amounts and becomes the main product at high temperatures (Figure 1 c & f). The propene formation indicates an acidic surface which is here introduced by the V sites. When water is present, propene formation is suppressed due to the competitive adsorption of water on these acidic sites. The incorporation of V in Co_3O_4 spinel thus offers a tool to tune the distribution of acidic sites affecting the selectivity.

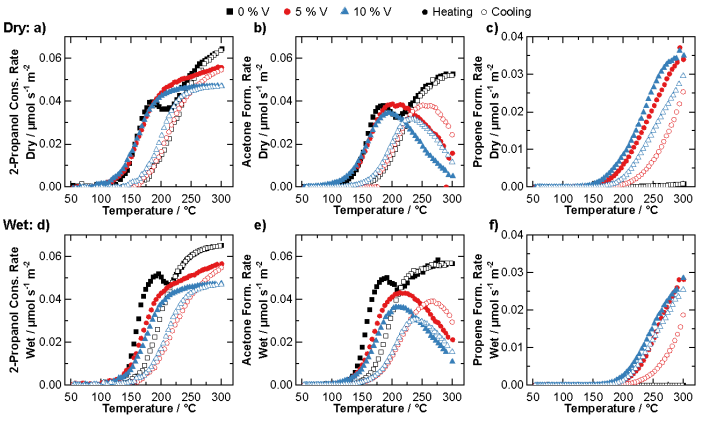

Figure 1: Trends in 2-propanol consumption (cons.), acetone and propene formation (form.) rates with V-doping in selective catalytic 2-propanol oxidation in dry feed (a-c) and wet feed (d-f).

Acknowledgments
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Ceria-supported mono- and bimetallic noble metal nanoparticles with narrow size distribution as model catalysts in emission control reactions

C. Schmitt[1*], J. Czechowsky[2], N. Da Roit[1], M. Casapu[2], S. Behrens[1]

[1]*Institute of Catalysis Research and Technology (IKFT) KIT, Eggenstein-Leopoldshafen, Germany*
[2]*Institute for Chemical Technology and Polymer Chemistry (ITCP) KIT, Karlsruhe, Germany*
[*]*christian.schmitt2@kit.edu*

Keywords: nanoparticle and cluster synthesis, noble metals, model catalysts, catalyst design, CO oxidation, exhaust gas treatment, continuous flow synthesis

Introduction. Nanosized transition metal particles are important materials in catalysis with a key role in academic research and in many industrial processes [1]. Pd- and Pt-based nanoparticles (NPs) supported on various metal oxides have been extensively employed as catalysts for various reactions, including emission control [2-4]. Due to their importance, there is a constant interest in optimizing their performance and reducing the noble metal loading. For their further development, relationships between catalyst structure and activity can only be revealed by studying well-defined catalysts. In the present study, mono- and bimetallic NPs with a narrow size distribution are prepared and used as precursors for catalysts in the oxidation of CO.

Experimental/methodology. The liquid-phase synthesis of well-defined, mono- and bimetallic NPs (Pt/Pd) is addressed in both batch and continuous processes. To prepare powder model catalysts, the particles are subsequently deposited on ceria. The NPs and catalysts are characterized, e.g. by electron microscopy (SEM, TEM, HAADF-STEM with elemental EDXS mapping), dynamic light scattering and atomic emission spectroscopy. The catalytic performance is investigated in CO oxidation, which is performed in a turbular reactor with a gas flow rate of 1 L min^{-1} of 1000 ppm CO and 8 % O_2 in N_2 [5].

Results and discussion. The Pd- and Pd-Pt NPs were spherical and monodisperse and uniformly distributed on the CeO_2 support (Figs. 1a, b and c). In general, different CO oxidation activity profiles were obtained for the mono- and bimetallic catalysts. For monometallic Pd-based catalysts, containing noble metal NPs of about 5-6 nm, the light-off temperature for CO oxidation was around T_{50}~120 °C (Fig. 1c), while the bimetallic catalyst showed a lower light-off temperature. Additionally, the systematic investigation of such powder model catalysts with defined size, shape, and composition revealed high stability for all prepared catalysts during consecutive CO oxidation cycles (see Fig. 1c)

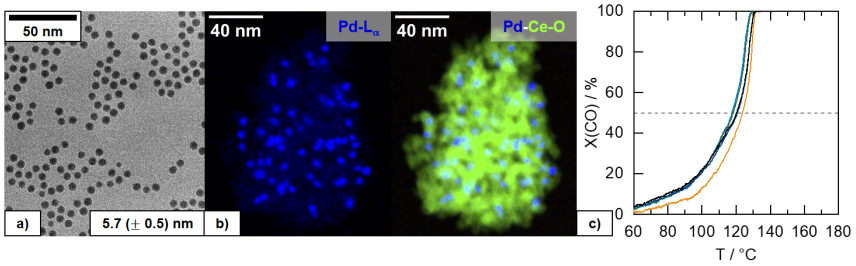

Fig. 1: a) TEM micrograph of Pd NPs; b) elemental EDS mapping of Pd and Ce and c) consecutive light-off curves of the Pd/CeO_2 catalyst during CO oxidation (1 L·min^{-1}; 1000 ppm CO; 8 % O_2 in N_2).

Acknowledgments
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Tandem Mixed-Metal Oxides/Zeolite Catalysts for CO_2 Utilization

C. Schroeder,[1] M. Palma,[1] N. Barrabés,[2] M. Sánchez-Sánchez[1],*

[1]*Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, Austria*
[2]*Institute of Materials Chemistry, TU Wien, Austria*
[*]*maricruz.sanchez@tuwien.ac.at*

Introduction. Direct catalytic CO_2 conversion into key chemicals is a promising field of research for sustainable processes. However, limitations exist for CO_2 utilization, i.e., its high activation energy. Tandem catalysts based on mixed metal oxides combined with zeolites (MO_x/zeolite) are suitable to combine CO/CO_2 hydrogenation on the metal/metal oxide function with the size selective C-C coupling catalyzed by acid sites within the zeolite micropores to produce highly demanded olefins.[1] In this work, we investigate the activation of CO_2 on selected MO_x/zeolite materials by testing their activity on the CO_2 conversion by reverse water gas shift reaction (rWGS, $CO_2 + H_2 \rightarrow CO + H_2O$). Oxygen vacancies on mixed-metal oxide surfaces are proposed to be relevant for the activity in both rWGS and CO_2 hydrogenation, therefore, we use the rWGS reaction as a proxy to evaluate the potential of the material for the tandem conversion of CO_2 into light olefins.

Experimental/methodology. Tandem $CuCeZrO_x$/SSZ-13 and $CuCeZrO_x$/ZSM-5 catalysts are either prepared by incipient wetness impregnation (IWI), or by co-precipitation (CP) in presence of sodium oxalate to prevent Cu^{2+} introduction in the micropores of the zeolite. Catalysts are then analyzed by X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), and temperature-programmed reduction (TPR) to assess loading, dispersion, and redox properties of Cu species. The kinetics of rWGS on the catalytic materials is investigated at a H_2:CO_2 ratio of 4:1, adequate for the overall syn-gas to olefins conversion, in a lab-scale differential reactor. On-line gas analysis is performed with gas chromatography.

Results and discussion. Reaction rates for rWGS reaction are roughly doubled when the oxides are supported on the zeolites. Characterization by TPR shows that peak reduction temperatures are generally lowered by 10 to 90°C for $CuCeZrO_x$ supported on zeolites compared to unsupported $CuCeZrO_x$ (220°C), which indicates more easily reducible Cu as a result of higher dispersion and support interactions.[2] For catalysts synthesized by IWI, peak reduction temperatures are lowered down to 100-140°C, while also a large portion remains oxidized even at 400°C, which is attributed to ion-exchanged Cu^{2+} on zeolite acid sites.[3] Oxalate in the co-precipitation method successfully prevents Cu^{2+} ion exchange at the expense of higher peak reduction temperatures. We have observed a correlation between reducibility of Cu species and activity for rWGS, even though, at the reaction conditions in H_2-rich atmosphere, Cu species are stable in metallic state. This suggests that the nature of interaction of Cu with the $CeZrO_x$ and zeolite supports have an effect in the generation of active sites for rWGS.

In conclusion, directly supporting $CuCeZrO_x$ on zeolites significantly boosts activity for rWGS compared to unsupported $CuCeZrO_x$. Although catalysts by IWI show the highest activity per Cu in this study, catalysts synthesized by oxalate co-precipitation are expected to perform better in the tandem conversion of CO_2 and CO into light olefins, because the acid sites of the zeolite are not affected by Cu in the micropores.

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Influence of Oxidative Fluorination on Cu/ZnO Methanol Catalysts for Carbon Dioxide Hydrogenation

H. Schuster[1*], I. Krossing

[1]*Materials Research Center, University of Freiburg, Germany*
[2]*Institute of Inorganic and Analytical Chemistry, University of Freiburg, Germany*
[*]*henrik.schuster@fmf.uni-freiburg.de*

Keywords: heterogeneous catalysis, methanol synthesis, CO_2 conversion, fluorination

Introduction: Ongoing global warming and abandonment of fossil fuels and feedstocks require a restructuring of the energy carrier profile. Using Cu/Zn synergism[1], catalysts can be developed that are suitable for converting the greenhouse gas carbon dioxide CO_2 and hydrogen H_2 into methanol MeOH, with perspective to a sustainable CO_2 cycle. Methanol has a wide range of applications, as it is an excellent platform chemical (for *e.g.* formaldehyde) as a C-source.[2] Furthermore, oxidative fluorination is used in the research group of Prof. Krossing to increase activity for methanol synthesis from CO_2 and H_2.[3]

Experimental/methodology: Oxidative fluorination was used to synthesize a series of precatalysts differing in their synthesis conditions and resulting fluoride content. Properties of the catalysts were studied by infrared spectroscopy IR, thermogravimetric analysis TGA, ion chromatography IC, powder diffraction pXRD and surface area quantification method N_2 physisorption. To determine the activity of the catalysts, the catalysts were activated with H_2 and subsequently feedgas CO_2 and 3 H_2 were fed at 210 to 270 °C at 40 bar. Catalysis products were quantified by gas chromatography GC. In addition, feed gas composition was varied between gas mixtures of CO/2 H_2 and CO_2/3 H_2 to investigate feed gas compatibility of the catalysts.

Results and discussion: Investigation by TGA and IR particularly show that oxidative fluorination has effects on high-temperature carbonates. Fluorination corresponds to a chemical calcination, the metal carbonates thereby form metal fluorides by release of CO_2 and O_2. pXRD patterns of the highly fluorinated systems show more crystalline phases than those of low or non-fluorinated precatalysts. Fluorination leads to the formation of more active sites on the catalyst surface and significantly increases the catalysts activity.[3] Furthermore, the selectivity for CO_2-to-MeOH conversion is increased, supporting the revolution from fossil sources (CO-to-MeOH) to recycling of CO_2.

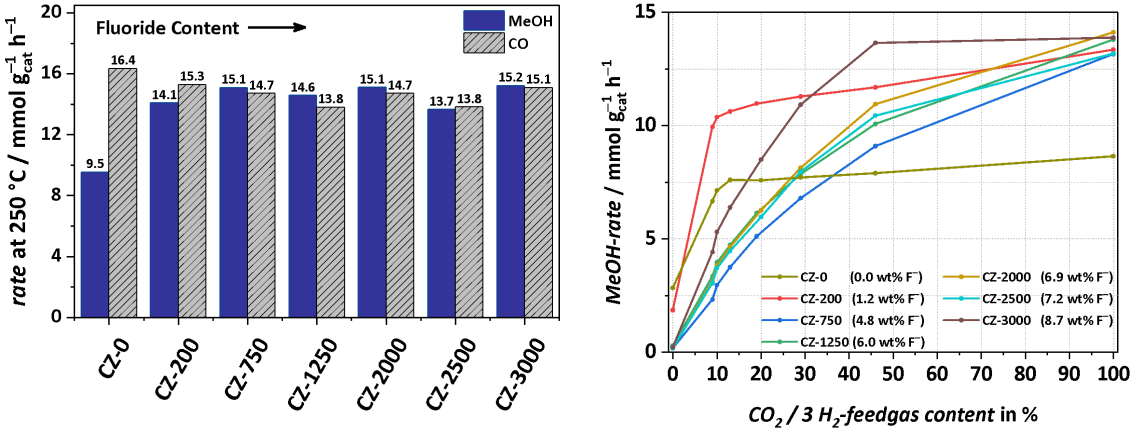

Figure 1: Catalyst testing of fluorinated catalysts. On the left side, catalyst testing has been carried out at 250 °C, 40 bar and 33 mL min^{-1}. On the right side, feedgas composition was varied from 100 % CO_2 / 3 H_2 to 100 % CO / 2 H_2 at 250 °C, 40 bar and 33 mL min^{-1} flow rate.

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Development of Hydroisomerization Catalyst for Diesel Fuel with Improved Cold Flow Properties

H. Schwarzová[1*], L. Meca[1], J. Jenčík[2,4] , J. Hájek[2,4], N. Heikkinen[3], M. Reinikainen[3]

[1]*Ranido, s.r.o., Prague, Czech Republic*
[2] *ORLEN UniCRE a.s., Litvínov, Czech Republic*
[3]*VTT Technical Research Centre of Finland, Espoo, Finland*
[4]*Department of Chemistry, Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences Prague, Prague, Czech Republic*
[*]*hedvika.schwarzova@ranido.cz*

Keywords: hydroisomerization catalyst, β-zeolite, fuel upgrading

Introduction. Finding an alternative fuel source to crude oil is a worldwide discussed topic.[1] Fischer-Tropsch (FT) process grants a route from carbon-rich solids to high-quality liquid fuel.[2] The drawback of FT process is a wide distribution of hydrocarbons chains length. The FT middle-distillate could be used as a diesel fuel; however, it contains high percentage of linear paraffines solidifying at low temperatures and cause a problem for its application during the winter season.

The aim of the research was finding a suitable catalyst that partially converts FT middle-distillates long-chained *n*-alkenes into branched *iso*-alkenes with limited hydrocracking. The desired upgraded product is characterized by improved cold flow properties (decreased CFPP value) and preserved cetane number above the standardized parameters.

Experimental/methodology. Serie of bifunctional catalyst samples based on a commercial β-zeolites and 0.5 % Platinum was prepared. The process of dealumination was applied on selected zeolites to adjust the silica-alumina ratio (SAR) and enhance the porous structure. Catalytic hydroisomerization testing was performed in a fix bed continuous flow reactor at constant WHSV and hydrogen flow. The effect of wide temperature range was investigated, followed by the evaluation of the optimal conditions for each catalyst sample.

Results and discussion. The goal of the project, to optimize CFPP value (up to -40 °C) of the fuel, was reached for several new catalysts.

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Propane Combustion over Alumina-Supported Copper Nanoparticles

K. Simkovičová[1,2,*], M. I. Qadir[1], N. Žilková[1], L. Kvítek[2] and Š. Vajda[1*]

[1] *Department of Nanocatalysis, J. Heyrovsky Institute of Physical Chemistry v.v.i., Czech Academy of Sciences, Prague, Czech Republic.*

[2] *Department of Physical Chemistry, Faculty of Science, Palacky University Olomouc, Olomouc, Czech Republic.*

* *karolina.simkovicova@jh-inst.cas.cz (KS), stefan.vajda@jh-inst.cas.cz (SV)*

Keywords: copper nanoparticles, aluminium oxide, catalytic combustion, propane

Introduction. The total combustion of volatile organic compounds is the most effective way to reduce their emission into the atmosphere. For this reason, the studies of the catalytic combustion of model compounds such as propane over economically and energetically inexpensive catalysts have also received considerable attention in green chemistry. In this regard, copper-based catalysts showed remarkable activity in the combustion of methane[1] and toluene[2]. In this work, the performance of two catalysts based on copper nanoparticles (Cu NPs) dispersed on nano, and bulk powder alumina supports in propane combustion to CO_2 was studied.

Experimental. The catalysts used for this study were prepared via wet impregnation of Cu NPs at 3 wt. % Cu loading on substrates of nano-Al_2O_3 (30-60 nm) and Al_2O_3 powder with pore size 580 nm. The prepared catalysts are therefore named Cu/nanoAl_2O_3 and Cu/Al_2O_3, respectively. The catalysts were characterised *ex-situ* with TEM, SEM and EDX before and after the catalytic test, AAS was performed on the as-made catalysts. The catalysts were tested in a quartz plug-flow reactor using PID Microactivity Set-up equipped with GC for the on-line detection of the products. The reactant mixture of propene and O_2 diluted in He was introduced at atmospheric pressure.

Results. Fig.1 shows TEM micrographs of as-made catalysts, their conversion and corresponding selectivities during propane combustion. Cu NPs, around 4 and 8 nm in diameter, were dispersed on nanoAl_2O_3 and Al_2O_3 supports, respectively. Both catalysts Cu/nanoAl_2O_3 and Cu/Al_2O_3 produce mainly CO_2 and propene, with the fraction of the latter dropping fast with increasing temperature, and Cu/nanoAl_2O_3 showing both higher conversion as well as higher combustion to CO_2 in comparison with Cu/Al_2O_3. Small amounts of ethane and ethylene were observed at 550 °C, with approximately 2 % methane and 3 % ethylene on Cu/nanoAl_2O_3, and 2 % methane and 6 % ethylene on Cu/Al_2O_3.

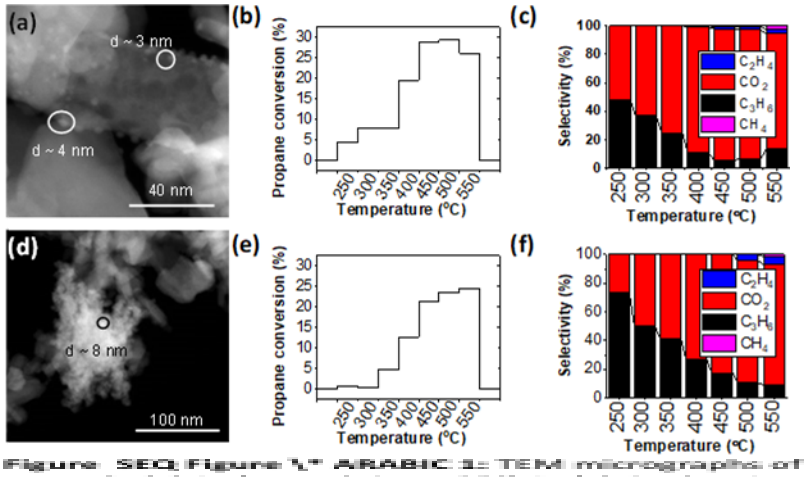

Figure SEQ Figure * ARABIC 1: TEM micrographs of as-made (a) Cu/nanoAl_2O_3 and (d) Cu/Al_2O_3 showing the Cu NPs, and their (b,e) conversion and (c,f) selectivity.

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Characteristics and Reactivity of Chelating N and O-donor Ru and Cu complexes in the oxidation of *n*-octane

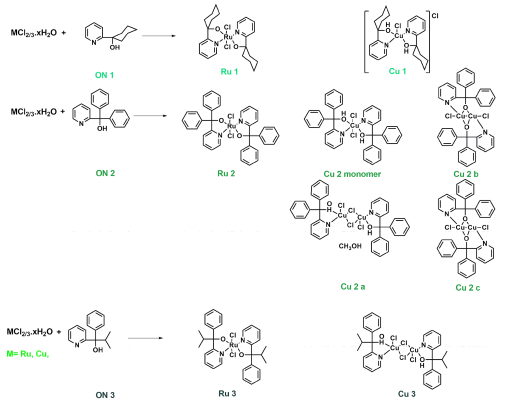
N.K. Singh[1*], L. Soobramoney[1], M.L. Shozi[1] and H.B. Friedrich[1]

[1]*University of KwaZulu-Natal, Durban, South Africa*
[*]*211501491@stu.ukzn.ac.za*

Keywords: catalytic oxidation of *n*-octane, ON bidentate ligands, crystal structures

Introduction. One of the most challenging areas of catalytic research in both academia and industry is the direct functionalization of C-H σ bonds of chemically inert linear alkanes[1-2]. Selective oxidations of linear alkanes is at the forefront of research to catalitically convert linear alkanes to value-added products. Biocatalytic systems, such as the heme-based cytochrome P_{450}, exhibit substrate specificity, regio and stereo selectivity and operate under mild conditions [3]. These systems have served as biomimetic inspiration for homogeneous catalytic selective oxidation of *n*-octane. In this study pyridinyl alcoholato ligands were coordinated to Ru and Cu and employed as catalysts in the oxidation of *n*-octane. Pyridinyl alcoholato ligands are bidentate ligands that bind to the metal centre via N and O donor atoms with the deprotonation of the O atom. This ligand imparts strong donor properties that can stabilize high oxidation states of metals and prevent ligand decomposition. These ligands can withstand harsh oxidizing conditions because they are tertiary alcohols[4-6].

Experimental/methodology. The combination of a solution of the respective ON ligands, in methanol with a solution of either copper or ruthenium chloride in a mixture of methanol and acetone resulted in the formation of neutral complexes, shown in scheme 1.



Scheme 1: The synthesis and coding of ON complexess

Results and discussion. The synthesised complexes were fully characterised. In the selective oxidation of *n*-octane the ruthenium complexes gave yields of 2-7 % to C8 oxygenates in 6 hours and selectivities of up to 70 % to C1-C4 alcohols, with H_2O_2 as oxidant. The copper catalysts gave yields up to 25% with predominant selectivity to C2-C4 ketones.

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Integration of Zeolite@Metal–Organic Framework: A Composite Catalyst for Isopropyl Alcohol Conversion to Aromatics

Omvir Singh [1,2*], Navneet Kumar Gupta[1] , Bipul Sarkar [2*]

[1]*Centre for sustainable Technology, Indian Institute of Science, Bangalore, Gulmohar Marg, Mathikere, Bengaluru, Karnataka 560012, India*

[2]*Catalytic Depolymerization Area, Upstream & Wax Rheology Division, CSIR- Indian Institute of Petroleum, Haridwar Road, Dehradun-248005, India*

**corresponding author: omvir10011995@gmail.com, bsarkar@iip.res.in,*

Keywords: Renwable aromatics, composite, zeolite, MOF.

Introduction

Aromatic production using bio-derived alcohols is desirable for various reasons. BTX from bio-derived alcohols is indistinguishable from traditional sources; therefore, the demarcation of end products is not required. In addition, the production of C_2–C_5 alcohol through sugar fermentation is high and continuously growing worldwide.1 Therefore, producing BTX from these alcohols provides a sustainable approach to promoting domestic resource consumption and foreign energy independence.

In this study, we designed a Zn-based MOF-zeolite composite by using an IRMOF-1 with a typical formula of Zn4O(BDC)3 and MFI type zeolite ZSM-5. The hybrid composite prepared from ZSM-5 and IRMOF-1 exhibits an Al/Zn ratio of ∼4 showed a dual distribution of ZSM-5 particles of ∼40-80 nm encapsulated within the MOF matrix and ZSM-5@IRMOF-1 particles of ∼40-50 nm located on the external surface of the composite. This composite features a combination of Nano pores and mesoporous, which may accelerate the mass transfer to enhance the aromatic yield compared to commercial ZSM-5. Our adopted strategy enhanced the Lewis acidic sites dispersed Zn-MOF composites paves the way for their evaluation as a durable aromatization catalyst.

Experimental/methodology.

The ZSM-5@IRMOF-1 composite was synthesised using a double-solvent strategy, where Zn $(NO_3)_2 \cdot 6H_2O$ (0.78 g, 3 mmol) and 1,4-BDC (0.165 g, 1 mmol) were dissolved in DMF (2 mL) as precursors for IRMOF-1. Subsequently, ZSM-5 (0.1 g) was suspended in dry n-octane (20 mL) as a hydrophobic solvent, and the mixture was stirred for 30 min. The hydrophilic precursor solution (0.1 mL) was added dropwise for 30 min with vigorous stirring. The resulting solution was continuously stirred at 120 °C for 24 h. After the solution cooled to room temperature, the supernatant was removed, and the solid deposited at the bottom of the flask was collected. The solid obtained was washed with DMF and dried overnight at 120 °C. The activity of aromatisation reactions was investigated in a fixed bed and continues down-flow reactor. 1 g of the palletised catalyst (40–60 mess) was placed between SiC beds into the reactor at 250–350 °C. Isopropyl alcohol (IPA) (feed) was introduced using a syringe pump at a flow rate of 0.5–4 h^{-1} (liquid hour space velocity, LHSV) and atmospheric pressure. The He gas was used as the carrier, and gas hour space velocity (GHSV) was maintained at 1200 h^{-1}. The product stream was separated through a glass condenser, and the gas was analysed using gas chromatography–refinery gas analyser (GC–RGA), Agilent Technologies equipped with an HP-PLOT Q column. Liquid hydrocarbons were analysed using the detail hydrocarbon analysis (DHA), Varian Inc., according to the ASTM D6730 test method.

Results and discussion.

Zn-composite materials and Zn-MOF have high surface area and coordinated unsaturated open metal sites, which may be useful for aromatisation. Table 1 presents the detailed product distributions of IPA to aromatics for different catalysts. In the presence of composite catalysts, aromatic hydrocarbons, mainly benzene, toluene, xylenes and ethylbenzene increased compared to Zn-supported ZSM-5 zeolite. This phenomenon may be correlated with the increase in the surface area, which can lead to the enhancement of metal dispersion on the catalyst surface. Another reason for enhanced aromatic selectivity may be the increased surface acidity with the modification of B/L ration caused by the replacement of BAS by Zn ions

(represents Lewis site) of MOF. Among these, Zn-composite provides the highest aromatic yield. Zn Comp. accounts for 92.3% conversion of IPA with 38.2% aromatic selectivity at 350°C, where the end product contain 4.8% benzene, 18.5% toluene, 11.3% xylene, and 3.6% EB.

Figure 1 presents the XRD patterns of IRMOF-1 (Zn-MOF), IRMOF-1@ZSM-5 (Zn-composite), and Zn-ZSM-5 (Zn/Z). The XRD patterns of crystalline IRMOF-1 shows the characteristic peaks at 2θ of 6.8^0, 9.6^0, and 13.7^0 that corresponded to (200), (220), and (400) crystal planes. This observed pattern agreed with the XRD diffractogram of IRMOF-1 reported by Luan et al.2 The XRD pattern of ZSM-5 in Zn/Z shows peaks at 2θ of 7.9, 8.9, 15.2, 17.2, and 19.4 corresponding to (011), (200), (501), (422), and (133) planes, indicating the crystalline hexagonal symmetry framework of the zeolite (JCPDS no. 49-0657, 2002 database).3 ZnO peaks appearing at 2θ of 34.4, 36.2, and 47.5 correspond to the (002), (101), and(102) planes of the hexagonal framework (JCPDS no. 36-1451, 2002 database)4. Incorporation of IRMOF-1 crystals in the ZSM-5 matrix, the XRD pattern showed distinct characteristics of both IRMOF-1 and ZSM-5, indicating the co-existence of IRMOF-1 on ZSM-5 channels.

The Zn composite (Zn-MOF supported ZSM-5) appeared as raspberry-like particles, where the outer shell is covered with needle-like spikes. The raspberry-like composites with a diameter of 1–1.5 µm exhibit a fluffy appearance compared with the morphology of ZSM-5 described in our previous studies. The HR-TEM analysis revealed (Figure 2) the presence of inter-grown 2-dimensional crystals of MOFs with a highly ordered rod-like structure having the size of a few hundred nanometres. Rare particles with the hexagonal ZSM-5 morphology were scattered inside the cavity but were not found on the outer surface. The image shows unclear fringes, which resulted from the collapse of MOF crystals during irradiation with high-energy X-ray used in TEM. The double solvent strategy is effective in incorporating mesopores in Zeolite@MOF composites, resulting in hierarchal materials.

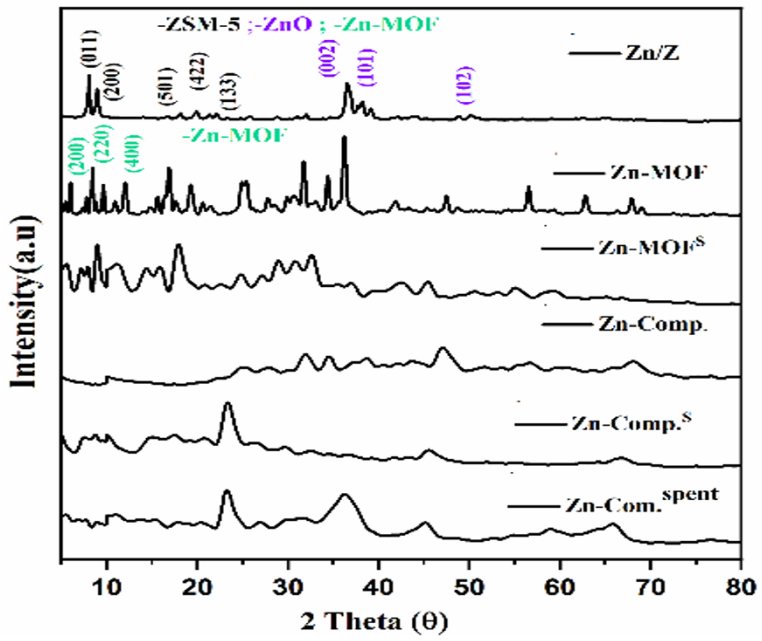

Figure 1: Powder XRD pattern of Zn-ZSM-5, different Zn-MOF and Zn-composite catalyst

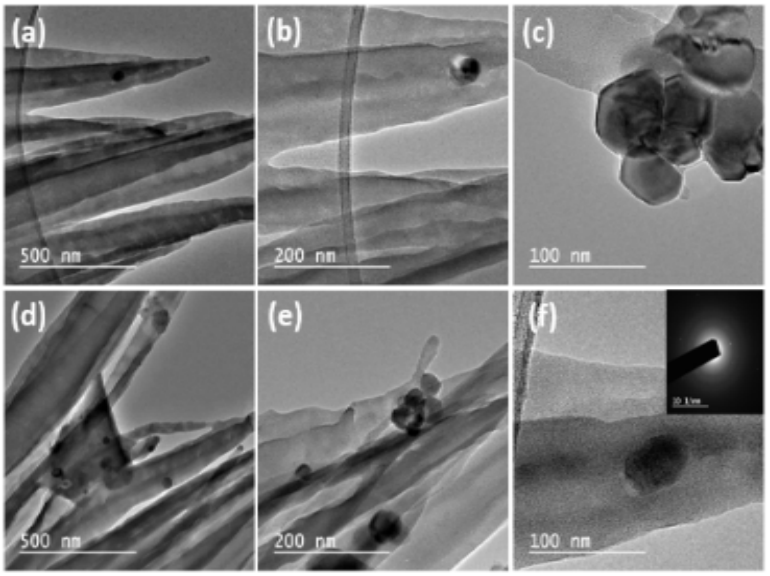

Figure 2: HRTEM with SAED image of Zn-composite catalyst.

Table 1. Comparative table for catalytic activities of different catalysts for liquid hydrocarbon distribution

S No.	Catalyst	Temp.	X_c (%)	Total BTEX	Product selectivity*					
					Benzene	Toluene	Xylene			EB
							o-	m-	p-	
1	Z-Zeolite	350	78.2	25.7	2.8	12.3	1.8	2.4	5.2	1.2
2	10Zn/Z	350	84.2	29.0	3.2	13.5	1.5	3.4	5.6	1.8
3	Zn-MOF	250	82.3	23.8	1.2	12.3	1.6	3.2	4.2	1.3
4	Zn Comp.	350	92.3	38.2	4.8	18.5	2.5	3.6	5.2	3.6

Reaction condition: Catalyst wt.-1 g (mesh size 50-70); reaction temp.-250-350°C; LHSV-2 h^{-1}; GHSV-1200 h^{-1}; time-after 6h

In summary, a catalytic Zn-based MOF-zeolite composite with tunable acidity, pore structure and better stability established for the first time. Different zinc composite materials using Zn-MOF with various zeolites were prepared using the double-solvent strategy. The systematic distribution of Zn sites in the MOFs framework led to an increase in the metal dispersion of the composite material. This large amount of exchanged Zn2+ species in IRMOF-1 enhanced the stability of the Zn-composite and increased its Lewis acidity. With the desired acidity and pore geometry, the new composite was found very active for isopropyl alcohol to aromatics. Based on activity data, the relationship between the catalytic activity and the features of a distinct increase in BET surface area, surface acidity and distribution of active sites in the framework have been investigated systematically. We anticipate that highly dispersed Zn on the composite exhibited a higher cyclodehydrogenation activity through isopropyl alcohol protonation and showed better performance than zeolites or MOFs. The present study might cover a new research method on interdisciplinary for Zeolite@MOF composite and other applications of these composites such as hybrid catalysis and enhanced gas adsorption.

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Light-driven coupling of acids and halides over a Ni single-atom catalyst

Mark Bajada,[1] Giovanni Di Liberto,[2] Sergio Tosoni,[2] Vincenzo Ruta,[1] Lorenzo Mino,[3] Nicolò Allasia,[1] Alessandra Sivo,[1] Gianfranco Pacchioni,[2] and Gianvito Vilé[1*]

[1]*Politecnico di Milano, Italy.* [1]*University of Milano-Bicocca, Italy.* [1]*University of Turin, Italy.*
[*]*Corresponding Author. E-mail: gianvito.vile@polimi.it*

Keywords: Single atom catalysis; flow reactors; heterogeneous catalysis; process intensification

Introduction. In recent years, the merging of photoredox chemistry and transition metal catalysis has attracted the attention of a growing number of researchers [1]. Unfortunately, most of the homogeneous (photo)catalysts and photoactive complexes to conduct these transformations (i.e., Ir and Ru-based complexes) suffer from sustainability issues, such as difficult purification of the mixtures, materials toxicity and costs, and catalyst recyclability. To bypass these challenges, we report herein a heterogeneous single-atom catalyst, merging peculiar features of homogeneous and heterogeneous analogues. The catalyst features single-atom Ni on mesoporous carbon nitride (Ni@mpgCN_x) for the direct coupling of alkyl halides and α-aminoacids. The intrinsic features of our optimally designed microreactor ensure improved homogeneity of light irradiation, that is always an issue for batch photocatalyzed protocols due to the limited contact between light, reactants, and catalyst.

Experimental/methodology. The catalyst was prepared following a three-step procedure. In brief, cyanamide, LUDOXTM, and $NiCl_2$ were mixed. The obtained solid was heated at 550 °C for 4 h. For flow experiments, different reactor geometries have been adopted. The solution was pumped by a syringe pump into the reactor irradiated using the PhotoCube reactor, with varying residence time values. For the comparative photocatalytic batch reactions, the bromo-derivatives and α-aminoacid were mixed in MeCN solvent and irradiated with white LED light at 40 °C (Photoreactor, ThalesNano) under a N_2 atmosphere. Isolated products were analyzed by ^{1}H and ^{13}C NMR, while conversions were monitored via HPLC.

Results and discussion. The catalyst characterization has been performed by combining a battery of analytical techniques, which confirmed the single-atom nature of the material. The catalyst was first tested in batch mode for the coupling of alkyl halides with α-aminoacids, in order to conduct a systematic study, and rationalize the effect that the wavelength of light, type of base, and solvent have on the kinetics of the system. The key driver behind the implementation of continuous flow technologies was the need to allow for a uniform radiation distribution inside the reactor, as dictated by the Beer-Lambert Law, which would maximize the efficiency of the photochemical process. For this reason, the optimal reactor design was based on a packed-bed architecture, which allowed for: (i) increased surface area-to-volume ratio, to satisfy homogeneity in the photon distribution, (ii) immobilization of both the solid photocatalyst and the base, by plugging these materials within the irradiated reactor zone. The presence of packing material made of borosilicate glass beads were deemed essential for separating the catalyst particles from one another (and improve light absorption), while simultaneously not being able to compete for incident visible-light photons. Such design alterations to the reactor allowed for an improvement of 20-25% in isolated yield relative compared to batch operation. Time-on-stream analysis confirmed the stability of our reactor configuration, and of the catalyst activity, while a scaled-up experiment performed at optimized conditions (white LED, T = 40 °C, τ = 20 min), elucidated the robustness of our protocol, and allowed to synthesize gram amounts of precursor compounds that have a direct relevance to the pharmaceutical industry.

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Preparation of Ni-Co-Mn mixed oxide coatings on stainless-steel supports by sol-gel method and their activity in oxidation of volatile organic compounds

T. Babii[a], K. Jirátová[b], J. Balabánová[b], F. Kovanda[a]

[a]*Department of Solid State Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague, Czech Republic*
[b]*Institute of Chemical Process Fundamentals of the CAS, Rozvojová 135, 165 02 Prague, Czech Republic*

Keywords: Ni-Co-Mn mixed oxides, sol-gel, supported catalysts

Introduction. Transition metals-containing oxides are widely used in heterogeneous catalysis as catalysts for various reactions such as dehydrogenation, selective oxidation, selective reduction, removal of volatile organic compounds (VOC) and electrocatalysis [1]. The performance of metal oxide-based catalysts depends on the methods and conditions of preparation. The sol-gel reaction is advantageous for the preparation of mixed oxide coatings combining various catalytically active components. The process involves the formation of a stable colloidal suspension (sol) by hydrolysis and partial condensation of reactants to form metal-oxygen-metal bonds [2]; products with a fine and homogeneous distribution of components are formed. The prepared sol can be deposited on substrates to obtain supported catalysts. The deposited gel contains relatively large amount of liquid and, after drying and calcination, oxide materials with a large surface area are obtained. The aim of this work was preparation of supported catalysts with catalytically active oxide coatings combining Ni, Co, and Mn components deposited on stainless steel supports. The precursors preparation by sol-gel method, their depoisition on supports, and thermal treatment were optimized to obtain homogeneous mixed oxide coatings with good adhesion to the stainless steel supports and good catalytic activity in VOC total oxidation.

Experimental/methodology. Ni-Mn, Ni-Co and Ni-Co-Mn mixed oxides coatings were prepared by sol-gel method. The salts (typically chlorides) of metals mentioned above were dissolved in distilled water together with complexing agent (tartaric acid) and water-soluble polymer (gelatin). The reaction mixture was stirred for several hours at 85-90 °C to evaporate water and obtain a desired volume of the mixture. The formed sol was deposited on the stianless steel substrates (sheets and meshes) by dip-coating method, dried in a controlled manner and finally calcined for 4 h at 500 °C in air. The obtained mixed oxides on the supports were characterized by powder XRD, Raman spectroscopy, and TPR and tested as catalysts in the total oxidation of ethanol, which was chosen as a model VOC.

Results and discussion. The combination of Ni, Co, and Mn chlorides, tartaric acid and gelatin in the reaction mixture for the sol-gel reaction led to the formation of a sol precursor suitable for deposition on the supports and obtaining of homogeneous oxide coatings after calcination. The adhesion of catalytically active mixed oxides to stainless steel sheets and meshes was improved by pre-coating them with SiO_2 interlayer and repeated dip-drying cycles before calcination. The deposited Ni-Mn coatings contained a mixture of Ni-Mn mixed oxides (Ni_6MnO_8 and $NiMnO_3$), whereas the spinel-type mixed oxides were found as a major component in the Co-containing samples. The supported mixed oxide catalysts with Co:Mn, Ni:Mn, and Ni:Co:Mn molar ratios of 4:1, 1:1, and 1:1:1, respectively, showed good catalytic activity in the ethanol deep oxidation.

Acknowledgments
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Oxidation of o-phenylenediamine by reactive oxygen species generated during H_2O_2 decomposition over composite oxide materials

K. Sobańska[1*], T. Smoliński[1], L. Wolski[2], P. Pietrzyk[1]

[1]*Faculty of Chemistry, Jagiellonian University, Krakow, Poland*
[2]*Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland*
[*]*kamila.sobanska@uj.edu.pl*

Keywords: Reactive oxygen species, o-phenylenediamine, oxidation, oxide catalysts

Introduction. The formation of reactive oxygen species (ROS) via the decomposition of hydrogen peroxide is associated with a cascade of reactions involving active redox centers of Fenton-like catalysts or acid-base functional groups of non-Fenton, amorphous surfaces of metal oxides that mediate electroprotic reactions [1]. These two catalytic functions can be achieved by combining two types of oxides, crystalline redox active oxides, and amorphous non-redox oxides, into one material. Such composite materials could be potentially used as catalysts in advanced oxidation processes (AOP), which are highly efficient and promising methods for the detoxication of wastewater. The present study aims to investigate the role of the reactive oxygen species in o-phenylenediamine (OPD) oxidation as a model AOP reaction.

Experimental/methodology. The composite oxide catalysts used in the study were synthesized using a hydrothermal method and characterized using XRD, XRF, zeta potential measurements, and Raman spectroscopy. The formation of ROS was monitored with Raman (peroxo species) and EPR (superoxide anions, hydroxyl radicals) techniques. Singlet oxygen was detected indirectly via oxidation with TEMP substrate (2,2,6,6-tetramethylpiperidine) into paramagnetic TEMPO and its detection with EPR. The chemical reactivity of the obtained materials was tested in the oxidation of OPD by using UV-vis absorption spectrometry.

Results and discussion. In this work, we have tested several oxide materials based on Nb_2O_5, CuO, CeO_2, combined into mixed, multiple oxide phases or composites with enhanced activity toward $^1O_2$ or radical ROS. We found this activity dependent on doping with phosphates or selected redox oxide nanocrystals. We have evaluated the role of hydroxyl radicals in OPD oxidation as well as the possible direct involvement of superoxide radical anions and singlet oxygen. Since oxidation of OPD is considered a test reaction for evidencing a peroxidase-like activity (oxidation with hydroxyl radicals) [2], we have concluded on the selectivity of OPD oxidation toward particular ROS substrates. For this purpose, the test reactions have been carried out for the mixtures containing catalyst suspension in water, OPD, H_2O_2, and typical quenchers of the individual ROS (alcohols, 1,4-benzoquinone, NaN_3).

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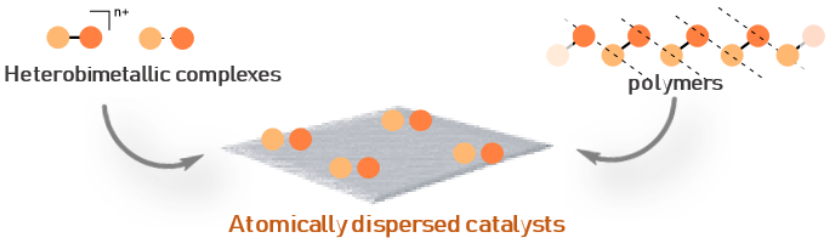
Defined precursors for atomically dispersed heterobimetallic catalysts

R. J. Somerville[1*], J.-C. Schmidt[1], P. J. Dyson[1]

[1] *Institut des Sciences et Ingénierie Chimiques (ISIC), Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland*
[*] *rosemarie.somerville@epfl.ch*

Keywords: single atom catalysts, heterobimetallic, catalyst design

Introduction.
Atomically dispersed single, double, and cluster catalysts are receiving intense research interest as class of catalyst that bridges the easy separation of heterogeneous catalysts with the tunability and single-site nature of homogeneous catalysts.[1],[2] However, their synthesis can be challenging, and limited options exist for the controlled formation of *heterobimetallic* or mixed-metal sites.[3] This leaves a gap where the fascinating reactivity of homogeneous bimetallic catalysts is difficult to explore in its atomically dispersed cousins.[4]
In this work, heterogeneous catalyst design and synthesis is linked with techniques from coordination chemistry to develop routes that install defined heterobimetallic sites on a support material.



Experimental/methodology.
Mixed palladium-platinum complexes were synthesised and a range of encapsulation and polymerisation techniques investigated to disperse the PdPt sites across support materials. The resulting materials were characterised by methods such as HAADF-STEM, XPS, ICP.

Results and discussion.

Coordination polymers and dispersed metal atoms were produced, resulting in mixed clusters and discrete double atom sites. These features were investigated by high resolution STEM. The catalysts were assessed in the electrochemical hydrogen evolution and CO_2 reduction reactions.

Acknowledgments
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Hydrogen purification for selective removal of oxygen: Deoxo catalysts

Youjung Song[1*], Sungtat Kim[2]

[1] *TheEN Co., Ltd. Daejeon, South Korea*

[2] *Department of Chemical Engineering and Applied Chemistry, Chungnam National University, Daejeon, South Korea*

[*] *songy.theen@gmail.com*

Keywords: Catalytic purification of H_2, deoxo-catalyst, H_2-O_2 recombination

Abstract

In complex and sophisticated devices using hydrogen as an energy source, the presence of impurities in hydrogen can cause fatal defects in the device. In particular, oxygen is an impurity that must be removed to ensure stability because there is a risk of explosion if more than 4% is present in the hydrogen stream. In this paper, we compared the performance of removing oxygen from the hydrogen stream using hydrogen-oxygen recombination reactions(eqn. 1) with various single metal catalysts.

$H_2 + ½\ O_2 \rightarrow H_2O$ ($\Delta_R H$) = - 242 kJ/mol (1)

The results of a study aimed at determining the feasibility of using catalytic deoxo-reaction to scavenge oxygen nearly zero from main gas stream. A series of experiments were conducted to assess the catalytic recombination characteristics and the catalyst that showed the highest performance was a catalyst using Pd. The result was that the oxygen concentration of 2% could be remarkabley lowered to about 5 ppm or less with metal loading of 0.1 wt.%. Furthermore, it was found that the catalyst maintained its performance even in a continuous reaction for 150 hours.

Acknowledgments

(optional,Calibri, 10 pt., Italic)

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Molecularly Defined Precursors for Pt Nanoparticle Controlled Growth and Speciation Targeting CO_2 Conversion

L. Sousa[1*], R. Guerra[1], G. Strapasson[1], C. Oliveira[1], D. Zanchet[1]

[1]*Institute of Chemistry – University of Campinas (UNICAMP), Campinas, Brazil*
[*]*l178387@dac.unicamp.br*

Keywords: Heterogeneous Catalysis, CO_2 Reduction, Coordination Compounds, Platinum.

Introduction.

Pt and TiO_2 present a dynamic interaction that can be understood by the strong metal support interaction mechanisms, which encompass (i) charge transfer at the interface between the metal and oxide; (ii) encapsulation, when a non-stoichiometric TiO_x layer cover the metallic nanoparticle; and (iii) alloy formation, when the system is over-reduced and Ti atoms are incorporated into Pt lattice [1]. We aim to employ organic complexes in the heterogenization of Pt on TiO_2 and evaluate how these precursors impact the dynamics of Pt/TiO_2 and the final catalytic performance in RWGS (reverse water gas shift).

Experimental/methodology.

The complexes were synthesized as described in Figure 1(a) [2]. They were impregnated on TiO_2 by wet impregnation and total Pt loading of 1 wt%. The pre-catalysts were pyrolyzed under $N_{2\,(g)}$ (500 °C for 1 h). XAFS (X-ray absorption fine structure) data were collected at BioXAS beamline (Canadian Light Source). For the RWGS reaction, 5 mg of catalyst mixed with a diluent was placed in a fixed bed tubular reactor. The RWGS reaction was performed with 2% CO_2, 8% H_2, and 90% He (total flow of 100 ml.min^{-1}, 500 °C for 1h).

Results and discussion.

Figure 1 (a) shows the synthesis of selected complexes. These compounds differ in their carbon content, and electronic structure, in which C2 and C3 have more carbon atoms, and C3 is an example of π-extended system. Figure 1(b) depicts the XAFS spectra of the complexes heterogenized on TiO_2 and pyrolyzed at 500 °C. The catalysts showed an intermediate electronic state, between Pt^{2+} and Pt^0 standards, indicating that pyrolysis reduced the samples but kept a certain degree of electron deficiency, with C1/TiO_2_P500 being the most reduced and C2/TiO_2_P500 the least. This difference had a clear impact on the catalytic activity for CO_2 conversion to syngas through the RWGS ($CO_{2\,(g)} + H_{2\,(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$), with C2/$TiO_2$_P500 having the highest conversion rate and C1/TiO_2_P500 the smallest one. We demonstrated that the design of molecularly defined precursors can be a promising strategy for modulating properties, such as metal speciation, particle size, and metal-support interaction. Complementary characterizations to XAFS and evaluation of other activation conditions (O_2, H_2) helped to understand the metal support interactions that take place among the complexes and TiO_2, we were able to identify a strong interaction through charge transfer and TiO_X formation at soft conditions (pyrolysis 350 °C), and its evolution under harsher treatments.

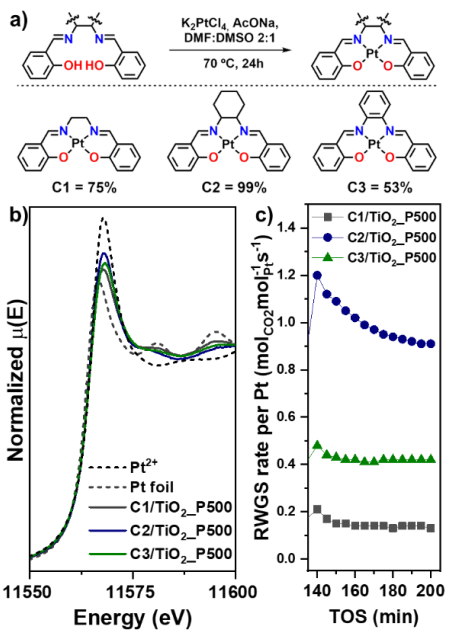

Figure 1. (a) Complexes' synthesis and yield; (b) XAFS spectra; (c) RWGS rate.

Acknowledgments

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Chemo-enzymatic C-H Bond Activation via *in-situ* H_2O_2 Production

A. Stenner[1*], R. J. Lewis[1], G. J. Hutchings[1]

[1]*Max Planck – Cardiff Centre on the Fundamentals of Heterogeneous Catalysis (FUNCAT), Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Translational Research Hub, Cardiff, CF10 3EY*

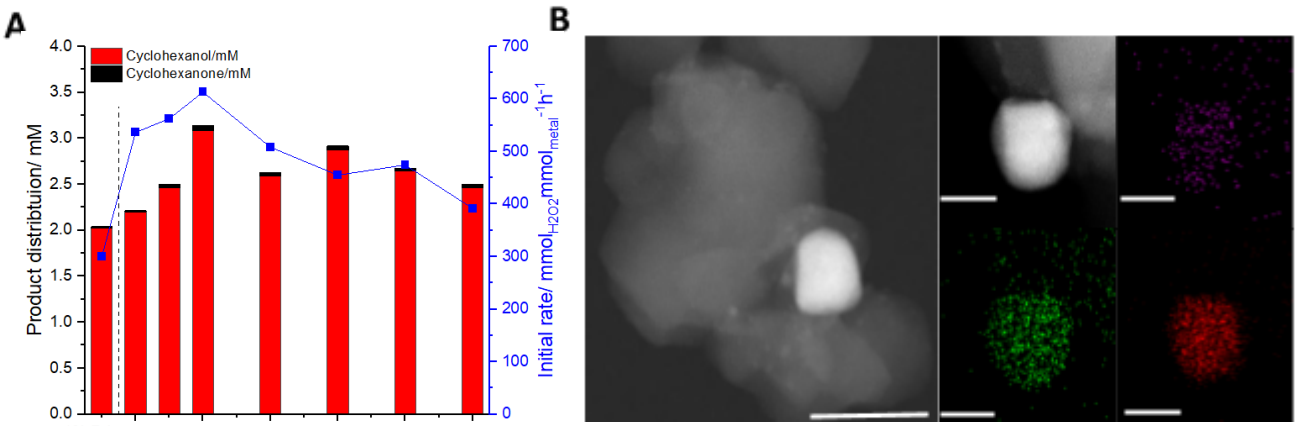
[*]*StennerAJ@cardiff.ac.uk*

Keywords: AuPdPt, Hydrogen peroxide, Peroxygenase, Cyclohexane, Oxidation, Cascade

Introduction. Combining an evolved unspecific peroxygenase, from *agrocybe aegerita* (PaDa-I variant), and 1 wt.% $Au_xPd_yPt_z/TiO_2$ chemo-catalysts in a one-pot system is demonstrated to be highly effective towards the selective hydroxylation of cyclohexane to cyclohexanol. The metal catalyst provides a continuous supply of H_2O_2 to PaDa-I via direct combination of H_2 and O_2. It is demonstrated that Pt alloying into AuPd nanoparticles (NPs) promotes the rates of H_2O_2 production, relative to the bimetallic analogue, leading to significant enhancement in process efficiency.

Experimental/methodology. Au-Pd-Pt/TiO_2 catalysts were prepared by a conventional wet impregnation procedure.[1] Cyclohexane oxidation cascade experiments were performed in a one-pot system under conditions conductive to enzyme stability.

Results and discussion. Incorporating Pt at dopant levels into AuPd NPs enhances the rate of H_2O_2 production, relative to Pd and AuPd analogues. Due to the rate limiting nature of *in-situ* H_2O_2 production when compared to the rate of enzymatic turnover, it is found that dopant levels of Pt enhance the activity of the oxidation cascade relative to the AuPd analogue, as shown in Figure 1A. An optimum Pt loading is found at 0.02 wt%, above which the rate of H_2O_2 production decreases. Notably,the high selectivity of PaDa-I towards the formation of cyclohexanol is preserved when the rate of H_2O_2 production is increased.



tion of chemo-enzyme oxidation cascade at 2 h reaction
ng in the $Au_1Pd_1Pt_x/TiO_2$ catalysts, and related to the initial
he catalysts under low-pressure conditions. **B)** AC-STEM
$_1Pd_1$-0.02%/TiO_2 catalyst.

Figure 1B shows AC-STEM and X-EDS imaging of the Au_1Pd_1-0.02%Pt sample and reveals the nature of Pt speciation, which exists almost exclusively in the AuPd alloys, resulting in the formation of trimetallic nanoalloys with size range 5 – 20 nm. The presence of well-dispersed monometallic Pd (~ 3 nm) is also observed, analogous to the AuPd sample. Through extensive characterisation it is demonstrated that the enhanced performance of the AuPdPt/PaDa-I system resutls from the electronic modification of the Pd species, as a result of Pt incorporation. These pbservations represent a considerable advance on previous works with this burgeoning field.

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Dimethyl ether as hydrogen carrier: Development of catalysts for DME steam reforming

R. Stöber[1], F. Seidl[1], P. Schühle[1*]

[1]*Institute of Chemical Reaction Engineering, Friedrich-Alexander Universität Erlangen-Nürnberg, 91058 Erlangen, Germany*

[*]*patrick.schuehle@fau.de*

Green hydrogen will play a key role in the defossilization of the global energy system. Hydrogen production from electrolysis, however, is economically only attractive where renewable electricity is available at low cost. Consequently, the locations for future large-scale electrolysis operations will in most cases not coincide with the hydrogen consumption sites, making the long-range transport a problem to be solved. Due to the low volumetric energy density of gaseous compressed hydrogen, conversion into easily liquefiable hydrogen carrier molecules like dimethyl ether (DME) is considered a solution [1]. While there are already commercial routes for the synthesis of DME, the reverse hydrogen release by DME steam reforming (SRD) still needs significant advances. The reaction proceeds over two steps, namely the acid catalysed hydrolysis of DME to Methanol, followed by methanol steam reforming (MSR) to CO_2 and H_2. For both individual reactions a variety of different heterogeneous catalysts finds application in literature [2]. For the first reaction step solid acids, such as H-zeolites or γ-Al_2O_3, are reported, while Cu/ZnO/Al_2O_3 or spinell-type catalysts are used for the MSR step [1]. However, coking and/or active metal sintering contribute to deactivation of these catalysts, especially when both reactions are combined in one setup [2]. Therefore, further catalyst development is required.

Figure 1: DME conversions of H-ZSM-5, γ Al_2O_3 and $Zr(HPO_4)_2$ over 8 h at 320°C

In this work, SRD catalyst studies were conducted in a continuously operated fixed-bed reactor (1 bar(g), 260-350 °C, H_2O:DME:N_2 of 5:1:2). In the first set of experiments, the stability of three different commercial acidic hydrolysis catalysts (H-ZSM-5, γ-Al_2O_3 and $Zr(HPO_4)_2$) was determined, without addition of a MSR system. To study the deactivation behaviour, catalyst masses (0,5 g of H-ZSM-5, 3 g of γ-Al_2O_3 and $Zr(HPO_4)_2$) were adjusted to avoid operation at the thermodynamic equilibrium. As can be seen from Figure 1, the HZSM-5 catalyst shows the highest (mass related) DME conversion at the beginning of the experiment, but deactivates over 8 h TOS. In contrast, the less acidic γ-Al_2O_3 and $Zr(HPO_4)_2$ show remarkable stability. Due to the best compromise of stability and activity, γ-Al_2O_3 was chosen for the combination with a reforming catalyst in subsequent studies.

A commercial Cu/ZnO/Al_2O_3 and self-synthesized supported Pd and PdZn catalysts (1 wt.% of Pd) were used for the screening of the reforming component. The materials were prepared by wet-impregnation of metal precursors on γ-Al_2O_3, followed by calcination and reduction. The catalysts were characterized by X-ray diffraction, ICP-AES and N_2-physisorption measurements before and after testing. A comparison of the investigated catalysts is given in Figure 2 (48 h TOS, 350 °C). Cu/ZnO/Al_2O_3 is the most selective of the screened materials, while the Pd catalysts favor CO formation. Higher hydrogen yields are observed with the Pd and PdZn systems. The addition of the Zn-Phase enhances the CO_2 selectivity of the Pd catalyst and

Figure 2: Hydrogen yields (△) and CO_2 selectivities (□) of the tested Pd/Al_2O_3 (blue), PdZn/Al_2O_3 (red) and Cu/ZnO/Al_2O_3 (grey) catalysts.

slightly improves catalyst stability, leaving room for further catalyst optimization.

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Transition metal-promoted LDH-derived CoCeMgAlO mixed oxides, active catalysts for methane complete oxidation

M. C. Stoian[1,2*], C. Romanitan[2], C. Negrila[3], H. Atia[4], K. Neubauer[4], I. Popescu[5], I.-C. Marcu[1*]
[1]*Laboratory of Chemical Technology and Catalysis, Department of Inorganic and Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, Bucharest, Romania*
[2]*National Institute for Research and Development in Microtechnologies, Voluntari, Romania*
[3]*National Institute of Materials Physics, Magurele, Romania*
[4]*Leibniz Institute for Catalysis (LIKAT), Rostock, Germany*
[5]*Division of Exact Sciences, Research Institute of the University of Bucharest, Bucharest, Romania*
[*]*Corresponding Authors. E-mail addresses: marius.stoian@imt.ro; ioancezar.marcu@chimie.unibuc.ro*

Keywords: layered double hydroxides, mixed oxide catalysts, methane combustion, VOC abatement.

Introduction. Different industrial processes produce flue gases containing volatile organic compounds (VOC) leading to air pollution and harmful effects over the environment, requiring treatment for VOC removal before release [1]. The most effective abatement process is catalytic combustion, whereas catalyst materials based on transition metal mixed oxides prepared from layered double hydroxides (LDH) precursors have shown great promise in this application [2]. We have previously shown that ex-LDH CoCeMgAlO mixed oxides are effective catalysts for the complete oxidation of methane, used as a VOC model molecule. The best composition was 40 at. % Co, 10 at. % Ce and Mg/Al atomic ratio of 3 [3]. Thus, in this work, two series of M-promoted CoCeMgAlO mixed oxides (M = Cu, Fe, Mn, Ni) were obtained from LDH precursors and tested for methane complete oxidation: a series of M(x)CoCeMgAlO mixed oxides with M content *x* = 3 at. %, and another series of Fe(x)CoCeMgAlO mixed oxides with various Fe contents *x* ranging from 1 to 9 at. % with respect to cations, while keeping constant in both cases 40 at. % Co, 10 at. % Ce and Mg/Al atomic ratio of 3.

Experimental/methodology. The mixed oxide catalysts were prepared *via* thermal decomposition at 750 °C of their corresponding LDH precursors obtained by coprecipitation. Their physico-structural properties were investigated with several techniques, such as XRD, SEM-EDX with elemental mappings, ICP-AES, XPS, H_2-TPR and nitrogen adsorption at -196 °C. They were tested in a fixed bed reactor for methane complete oxidation with a gas feed of 1 vol.% methane in air.

Results and discussion. XRD analysis revealed in all the samples the coexistence of Co_3O_4 crystallites with periclase-like and ceria phases, with no separate M-based oxide phase. All the cations are homogeneously distributed in the mixed oxide as suggested by EDX measurements and elemental mappings of the samples. The metals contents were determined by EDX and ICP-AES and were in accordance with the theoretical values set for the preparation of the catalysts. The redox properties studied by H_2-TPR, along with the surface composition determined by XPS have provided information to elucidate the catalytic behavior of the investigated materials. The catalytic tests have shown that all the M-promoted CoCeMgAlO mixed oxides are more active than their M-free counterpart. The highest promoting effect was observed for Fe. The Fe(x)CoCeMgAlO mixed oxide sample, with *x* = 3 at. % Fe, displayed the highest catalytic activity for methane combustion with a temperature corresponding to 50 % methane conversion, T_{50}, of 489 °C, which is ca. 40 °C lower than that of the unpromoted catalyst. This was attributed to its superior redox properties and lowest activation energy among the studied catalysts, likely due to a Fe-Co-Ce synergistic interaction. In addition, long term tests of Fe(3)CoCeMgAlO mixed oxide has been examined showing a good stability over 60 h on-stream. On the other hand, the addition of water vapors in the feed led to textural and structural changes of the Fe(3)CoCeMgAlO system affecting its catalytic performance. At the same time, the catalyst recovered its catalytic activity as soon as the water vapors were removed from the feed.

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Acidity modulation impact over metal-support interactions of Pt-supported catalysts

G. B. Strapasson[1,2*], L. S. Sousa[1], G. B. Báfero[1], D. S. Leite[1], C. B. Rodella[2], D. Zanchet[1]

[1]*Institute of Chemistry, University of Campinas, UNICAMP, Campinas, SP, Brazil*
[2]*Brazilian Synchrotron Light Laboratory, CNPEM, Campinas, SP, Brazil*
[*]*g216373@dac.unicamp.br*

Introduction. Understanding how to tune the properties of metal oxides, e.g. controlling and manipulating defects and catalytic sites, and establishing a clear understanding of metal-support interactions is essential for developing catalysts with enhanced activity, selectivity, and stability. Reducible metal oxide supports, that associate redox and acid properties, in combination with a metallic phase, can result in promising catalytic systems for different reactions. The hydrodeoxygenation (HDO) reaction is one of the main biomass-derivate upgrading processes to obtain biofuels and deals with the selective cleavage of C-O bonds under a hydrogen-rich atmosphere combined with a solid catalyst, reducing the oxygen content to produce hydrocarbons as the main products. Here, Ti-Nb mixed metal oxides were explored to address the impact of acidity in HDO reaction.

Experimental/methodology. Ti-Nb mixed metal oxides with various Nb at.% contents were synthesized using a hydrothermal methodology. Pt-supported catalysts were obtained through the wet impregnation method over 0 at.% Nb and 25 at.% Nb supports. Vapor phase acetone HDO reaction was conducted in a plug-flow tubular reactor equipped with a quartz tube. Textural, structural, and electronic characterizations of the catalysts were conducted using various techniques.

Results and discussion. The formation of Ti-Nb mixed metal oxides was achieved up to 25 at.% Nb (Ti:Nb), where morphological and structural modifications were verified upon Nb insertion into the TiO_2 anatase crystal lattice, according to SEM, XRD, and short- and medium-range order PDF analysis. Py-FTIR and ^{31}P NMR of adsorbed TMPO demonstrated that Brønsted/Lewis (B/L) acid sites ratio increased along with the Nb content (Figure 1a). The acid site distribution per accessible area in all mixed oxides presented similar values, between 0.28 and 0.41 sites per nm^2. The impact of the acidity modulation of these materials was evaluated using Pt-supported catalysts in the acetone HDO reaction. While the dominance of Brønsted acid sites led to 60 % of deoxygenated products (DOD - degree of deoxygenation) along 20 h on stream, the dominance of Lewis acid sites led to a DOD about 3 times smaller (Figure 1b). XPS measurements of pre- and post-reaction Pt-supported catalysts indicated that the Pt dispersion and Pt species differed depending on the support. The presence of Nb led to more oxidized Pt species and better dispersion. These oxidized Pt species decreased the coke deposition, resulting in more stable metallic sites. The catalytic performance demonstrated that Pt-supported catalysts with selective C-O bond cleavage could be designed through the modulation of catalytic sites of the support. We also demonstrated that the acidity modulation of the support led to significant changes in the metal-support interaction (MSI), affecting both the nature and stability of the catalytic sites. A better understanding of the correlation between acidity and MSI effects of Pt-supported over metal oxides could be provided, along with a correlation with the catalytic performance.

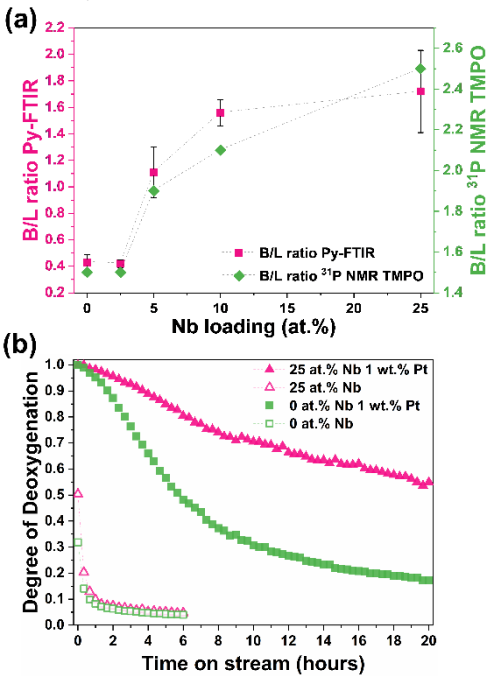

Figure SEQ Figure * ARABIC 1: (a) B/L acid sites ratio measured by Py-FTIR and ^{31}P-NMR of adosrbed TMPO; (b) DOD over TOS for the Pt-supported catalysts and their bare supports.

Acknowledgments

We thank FAPESP (2018/01258-5, 2020/12986-1, and 2020/08575-6), CNPq, and CAPES for funding.

Synergistic Catalysis between Fe Single Atoms and Fe_3O_4 Nanoparticles to Generate Reactive Oxygen Species for the Oxidative Trifluoromethylation of Olefins

Tianyue Su, [1] Chun Cai [1*]

[1] School of Chemistry and Chemical Engineering, *Nanjing University of Science & Technology, Nanjing, China*
[*] *Corresponding Author's E-mail: c.cai@njust.edu.cn*

Keywords: Fe single atoms; Fe_3O_4 nanoparticles; synergistic effect; reactive oxygen species; the oxidative trifluoromethylation.

Introduction

In recent years, the α-trifluoromethylated ketone compounds have been well considered as valuable building blocks for the construction of fluorinated products. The traditional synthetic strategy using olefins as substrates and CF_3SO_2Na as CF_3 source is photoredox catalysis, but it's limited by the light source, high price, toxicity or large-scale application etc. Therefore, the development of thermal-driven heterogeneous methodology to obtain α-trifluoromethylated ketones under mild conditions is highly imperative.

Experimental/methodology

The addition of aniline and ammonia during the synthesis of Fe-ZIF-8 precursors can effectively adjust its morphology, crystallization rate and the particle size. Besides, the BAN-Fe@NC catalyst by ball milling method have a better catalytic performance than the general Fe@NC catalyst and the reaction condition which is carried at 80 ℃ for 12 h under 1 atm O_2 atmosphere is green and sustainable.

Results and discussion

We discovered the coexistence of Fe_3O_4 nanoparticles with Fe single atoms on the N-doped porous carbon nanotube could significantly improve catalytic performance for the oxidative trifluoromethylation of olefins using O_2 as the oxidant (Figure 1). The optimal BAN-Fe@NC catalyst has exhibited a high efficiency with a broad substrate scope under mild conditions. Furthermore, it could be easily recovered because of its magnetic properties and reused 5 run without appreciable loss of activity. Experimental measurements and mechanistic studies revealed that both the superoxide radicals ($O_2^{\cdot-}$) and the singlet oxygen ($^1O_2$) were the main reactive oxygen species (ROS), and this catalyst structure has a great influence on the absorption of O_2 and the ability of thermally-driven generating ROS, which are attributed to the "synergistic effect" between Fe_3O_4 nanoparticles and Fe single atoms. It not only offers a simple method in the design of Fe catalysts but also opens up a heterogeneous pathway for the oxidative trifluoromethylation of olefins *via* radical mechanism.

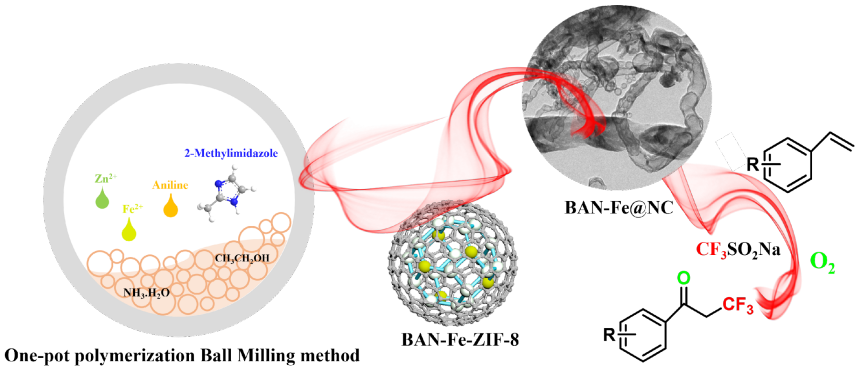

Figure 1. the preparation of BAN-Fe@NC and its catalytic application in the oxidative trifluormethylation of olefins (B is ball-milling method; A is aniline; N is ammonia).

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Water-Soluble NHC-stabilized PdNi Nanoparticles for H/D Exchange in Aromatic Amino-Acids

O. Suárez-Riaño[1*], G. Mencia,[1] S. Tricard,[1] B. Chaudret,[1] E.A. Baquero.[2]

[1]*LPCNO, Laboratoire de Physique et Chimie des Nano-Objets, INSA, CNRS, UPS, Université de Toulouse, 135, Avenue de Rangueil, F-31077 Toulouse, France*

[2]*Estado Sólido y Catálisis Ambiental (ESCA), Departamento de Química, Universidad Nacional de Colombia, Carrera 30 Nº45-03, Bogotá D.C., Colombia*

[*]*e-mail: suarez-riano@insa-toulouse.fr*

Keywords: Palladium, Nickel, Bimetallic Nanoparticles, H/D Exchange, N-Heterocyclic Carbene

Introduction.

Deuterated amino-acids have gained importance in recent years due to their application in deuterated proteins production. The smart way to obtain these molecules is through direct H/D isotopic exchange by means of C-H bond activation. Although nanocatalysts based on Ni, Ir, Ru, Pd and Pt have shown good performance on this reaction, aromatic amino-acid reduction is a common undesired process.[1] In order to overcome this drawback, we present here PdNi-based nanoparticles (NPs) stabilized by a hydrophilic (**IMesPrSO$_3$**) N-Heterocyclic Carbene (Figure 1) as nanocatalysts for H/D exchange. We have found that **PdNi@IMesPrSO$_3$** selectively deuterate aromatic amino-acids such as L-phenylalanine and L-tyrosine without reduction of the aromatic ring in an enantiospecific fashion thanks to a synergetic Pd-Ni effect.

Experimental/methodology.

Mono- and bi-metallic NPs of Pd and Ni were synthesized by the organometallic approach method using $Pd_2(dba)_3$ and $Ni(COD)_2$ as metal precursors and **IMesPrSO$_3$** as stabilizing agent (Figure 1).[2] The NPs were characterized by state-of-the-art of techniques (TEM, HR-TEM, XRD, XPS, ATR-FTIR, SS-NMR) and used as nanocatalysts in H/D exchange over L-phenylalanine (PhAla) and L-tyrosine (Tyr).

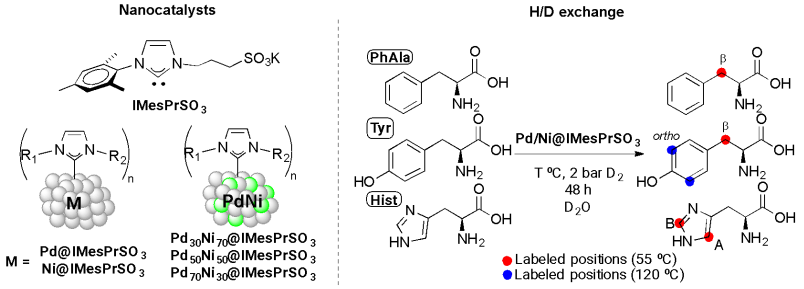

Figure 1. Pd, Ni and PdNi NPs stabilized by **IMesPrSO$_3$** and their use as nanocatalysts in HIE reactions.

Results and discussion.

Solid-state NMR and XPS techniques allowed us to confirm the NHC coordination to the PdNi NPs surface, which explains their high colloidal stability found in water. In addition, we were able to confirm the bimetallic nature of the PdNi NPs by XRD, STEM-EDX and ATR-FTIR techniques. Regarding the catalytic activity, while monometallic Pd and Ni NPs displayed low deuteration values, bimetallic PdNi NPs (**Pd$_{70}$Ni$_{30}$@IMesPrSO$_3$**) showed great deuterium incorporation values (up to 98.5%) at the CH_2-β position of PhAla without aromatic reduction. This behavior is explained by a Pd–Ni synergetic effect. On the contrary, Tyr showed a different behavior and the selectivity of the deuteration was found to be temperature-dependent. These results together with the enantiospecificity found for the first H/D exchange in PhAla and Tyr will be also discussed.[3]

Acknowledgments

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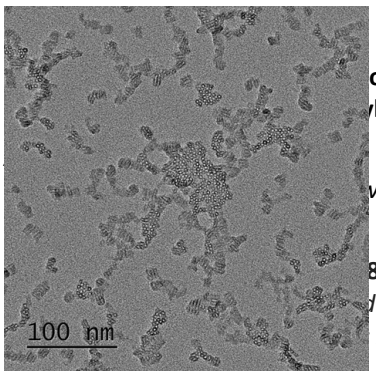
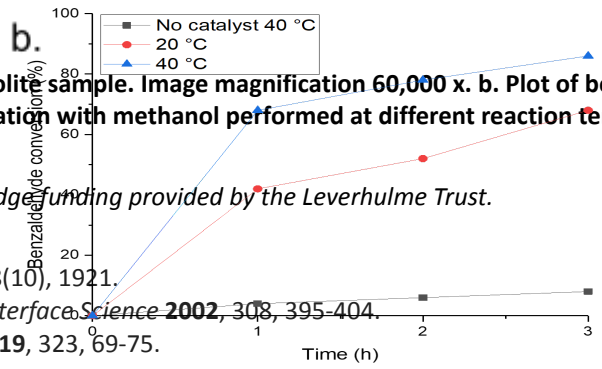
Assessing the catalytic capabilities of Ge-Imogolite nanotubes

L. Bailey[1], T. Davies[1], A. Graham[2], S.Taylor[1]*

[1]*Cardiff Catalysis Institute, Cardiff University, Cardiff, CF24 4HQ, UK*
[2]*School of Applied Sciences, University of South Wales, Upper Glyntaff, CF37 4AT, UK*
[*]*taylorsh@cardiff.ac.uk*

Introduction. Imogolite ($(OH)_3Al_2O_3SiOH$) is a naturally occurring aluminosilicate clay mineral possessing a nanotubular structure, typically having a diameter of 2 nm with a length of several hundred nanometers. Limited study has been performed on characterising and the application of this material. It is currently proposed that imogolite could find success as a molecular sieve or by reinforcing polymers through formation of a nanocomposite material [1]. It has also been proposed the imogolite could find application as a catalyst due to the gibbsite structure of the outer wall displaying acidic and basic properties [2]. Investigations into imogolite as a catalyst for glucose to fructose isomerisation has proved successful [3]. DFT studies have also suggested it would make a successful photocatalyst. Imogolite has shown versatility with several possible modifications explored. Germanium and iron have both been substituted into the structure while both the inner and outer surface of the nanotube has been functionalised [3]. This work aims to investigate a methods of synthesizing germanium-imogolite and its suitability as a catalyst.
Experimental/methodology. A stock solution of aluminium nitrate nonahydrate and germanium ethoxide was refluxed for 4 days with the solution subsequently dialysed and dried to give a powder. The material was characterized primarily using electron microscopy, porosimitry, and acidity measurements. Catalytic testing was performed through liquid-phase acetalization of benzaldehyde with methanol.
Results and discussion. Ge-imogolite types were successfully synthesised using this method. Unlike previous studies into this material where a mixture of nanotube lengths were seen often reaching 100 nm, microscopy identified a very regular length of 8 nm. This was consistent across syntheses and reflux times identifying this as a technique to synthesise nanotubes with reliable and expected properties. Porosimitry was performed identifying a double-walled nanotube with an inner diameter of 2 nm and outer diameter of 4 nm. Material acidity was also gauged via NH_3-TPD and pyridine DRIFTs showing a high number of acid sites, especially when compared to other aluminosilicates. Initial catalytic testing investigated the Ge-imogolite for the acetylisation of benzaldehyde with methanol showing high conversion after 1 hour at ambient temperatures. This suggests that Ge-imogolite could find use as an active catalyst. Further study into Ge-imogolite's catalytic capabilities along with its use as a support for metal nanoparticles is in progress.





ogolite sample. Image magnification 60,000 x. b. Plot of benzaldehyde conversion
vlisation with methanol performed at different reaction temperatures.

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Pt/CeO_2, Pt/TiO_2 and Pt/TiO_2-CeO_2 catalysts prepared by using titanyl sulphate in oxidation of dichloromethane

A. Šlachtová[1*], I. Troppová[1], S. Pitkäaho[2], L. Matějová[1]

[1]*Institute of Environmental Technology, CEET, VSB-Technical University of Ostrava, 17.listopadu 15/2172, Ostrava-Poruba, Czech Republic*
[2]*Environmental and Chemical Engineering Unit, Faculty of Technology, University of Oulu, P.O.Box 4300, FI-90014 University of Oulu, Finland*
[*]*adela.slachtova@vsb.cz*

Keywords: chlorinated VOC, dichloromethane, catalytic oxidation, titania-ceria, titanyl sulphate

Introduction. Emissions of volatile organic compounds (VOCs) into air and water from processes and products are considered as serious environmental problem [1,2] . According to the classification of the International Agency for Research on Cancer some of widely used VOCs belong to the three most serious groups; group 1 (carcinogens, *e.g.* formaldehyde, vinyl chloride), group 2A (probable carcinogens to humans, *e.g.* halogenated VOCs such as dichloromethane, perchloroethylene) and group 2B (possible carcinogens to humans, *e.g.* acetaldehyde, halogenated VOCs such as chloroform) [3]. Emitted VOCs can also react with other gases and particulates, forming secondary air pollutants being even more harmful, moreover, complicating their abatement. Catalytic combustion is a well-accepted and reliable technology for industrial VOCs abatement in environmentally and economically acceptable manner.

Experimental/methodology. A set of Pt/CeO_2, Pt/TiO_2 and Pt/TiO_2-CeO_2 catalysts with various molar composition (Ti:Ce – 9:1, 7:3, 5:5, 3:7) was prepared by co-precipitation method using titanyl sulphate as Ti precursor, impregnation and calcination. Catalytic oxidation experiments were carried out on a laboratory apparatus consisting of a flow-through tube reactor with a fixed catalyst bed located in the furnace, injection of dichloromethane (500 ppm) with water (1.5 wt.%) and an on-line FTIR analyzer. The efficiency of catalysts in oxidation of dichloromethane was studied in the range of 100−500°C, under the SV of 70 $m^3 \cdot kg_{cat}^{-1} \cdot h^{-1}$.

Results and discussion. Over all investigated catalysts 100% conversion of dichloromethane was reached. Pt/TiO_2 and $Pt/Ti_{0.7}Ce_{0.3}O_n$ showed the best catalytic activity. Pt/TiO_2 showed also the highest HCl selectivity. It was found out that catalysts prepared from titanyl sulphate precursor contain sulphates, which affected the acidity of the catalysts, being a determing property in the first adsorption step within dichloromethane oxidation. Increased reducibility of catalysts due to present Pt species was reflected to improved CO_2 selectivity.

Acknowledgments
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Effect of Cu/Ce Ratio on Benzene Oxidation over Gold-promoted Alumina-supported CuO-CeO_2

T. Tabakova[1*], P. Petrova[1], Y. Karakirova[1], G. Avdeev[2], E. Kolentsova[3], L. Ilieva

[1]*Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*
[2]*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*
[3] *Department of Chemistry and Phytopharmacy, Agricultural University, 4000 Plovdiv, Bulgaria*
[*]*Corresponding Author's E-mail address: tabakova@ic.bas.bg*

Keywords: gold catalysts, Cu-Ce mixed oxide; complete benzene oxidation

Introduction. Nowadays, the increased levels and detrimental effects of volatile organic compounds (VOCs) on air quality and human health have become a serious global concern from environmental point of view. A variety of technologies is applied to decrease harmful emissions from various chemical industries. Among them, complete oxidation to CO_2 and water at relatively low temperature is one of the most effective and environmentally-friendly approach for VOCs removal. Rational design of catalytic materials with high effectiveness in the destructive elimination of VOCs is one of the scientific challenges. It has triggered a substantial interest in the field of environmental catalysis because efficient catalysts should combine high activity and economic profitability. Currently, two major types of catalysts, namely noble metal-based and transition metal oxides are the most intensively studied to meet demanding environmental regulations. The aim of the present work is to study complete benzene oxidation (CBO) over Al_2O_3-supported CuO-CeO_2 mixed oxide promoted by gold. The investigation is focused on the effect of various Cu/Ce molar ratios on benzene conversion. Benzene molecule is the most stable among the aromatic hydrocarbons with toxic and often carcinogenic effect known as BTEX (benzene, toluene, ethylbenzene, and xylenes) owing to the symmetry and stability of the benzene ring.

Experimental. Wet impregnation of γ-Al_2O_3 with solution of $Cu(NO_3)_2.3H_2O$ and $Ce(NO_3)_3.6H_2O$, properly mixed to guarantee Cu:Ce molar ratio of 2:1 and 1:5 in the composition (20 wt.% active phase in total) was used for sample preparation. Synthesis of gold-containing (2 wt.%) samples on water suspended carriers by using ultrasound was performed by deposition-precipitation. Analysis of the impact of support composition in benzene oxidation was based on sample characterization by textural measurements, PXRD, EPR spectroscopy, and TPR technique.

Results and discussion. Complete oxidation of benzene as a probe reaction for VOCs elimination over alu-mina-supported CuO-CeO_2 mixed oxide promoted by gold was studied. The effect of various Cu/Ce ratios, namely 2:1 and 1:5, and the role of supported gold nanoparticles were investigated. Catalytic activity was greatly influenced by sample composition. Catalytic tests demonstrated that the Cu-Ce 1:5 configuration outperformed the catalytic behavior of the single-component counterparts in the whole temperature interval, while Cu-Ce 2:1 exhibited such behavior above 250 °C. Incorporation of Cu ions into the ceria lattice was proven by a small shift of the ceria main XRD peak in the patterns of all Cu-Ce containing samples evidencing defect formation, in particular Ce^{3+} ions and oxygen vacancies. Promotion by gold provided additional benefits to the benzene conversion. Gold on alumina-supported binary oxide catalysts exhibited a substantially higher activity than promoted supported monometallic oxides. Our findings revealed a crucial role of highly dispersed CuOx for benzene oxidation activity. The highest concentration of paramagnetic Cu^{2+} ions and the best dispersion of CuO in Cu-Ce 1:5 and Au/Cu-Ce 1:5 correlate well with best performance among alumina-supported oxides and gold-containing catalysts, respectively. Gold nanoparticle availability contributed to enhanced mobility of oxygen in ceria surface layers, thus facilitating the process of oxygen vacancy formation and replenishment. Au/Cu-Ce 1:5 achieved stable total oxidation to CO_2 and water by 94 % benzene conversion at 250 °C, thus implying the potential of this composition in developing efficient catalytic materials for atmospheric pollutant abatement.

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Liquid-phase catalytic oxidation of alcohols over spinel oxides

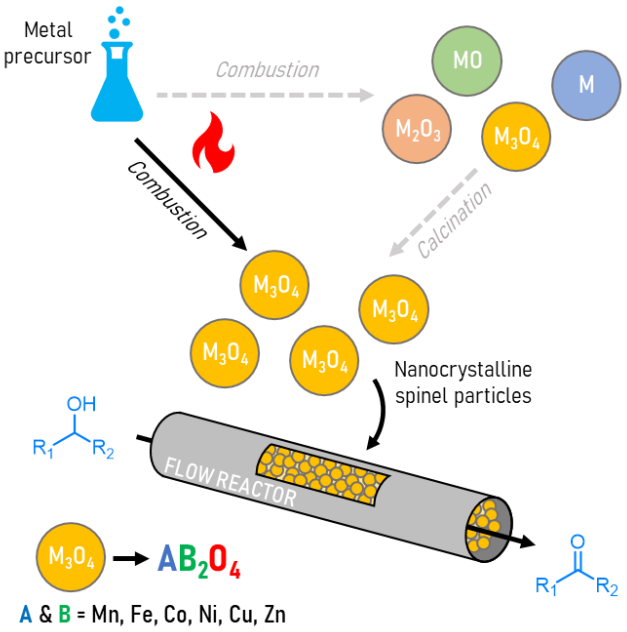
A. Tampieri[1], F. Romanelli,[1,2] T. Lederer[1], M. Pittenauer[1], K. Föttinger[1*]

[1]*Institute of Materials Chemistry, Technische Universität Wien, Vienna, Austria*
[2]*Polytechnic University of Milan, Milan, Italy*
[*]*karin.foettinger@tuwien.ac.at*

Keywords: Spinel oxides, alcohol oxidation, nanocrystals, flow reactor, solid-liquid interface.

Introduction. The selective oxidation of alcohols is an important synthetic tool in the portfolio of the chemical industry. Even though the oxidation of small alcohols such as methanol to formaldehyde are established processes, the selective transformation of higher alcohols is more challenging; moreover, the mechanistic understanding of these reactions over heterogeneous catalysts is still poor, especially about the phenomena taking place at the solid-liquid interface [1]. Besides, the most active catalysts are based on noble metals [2]; metal oxide catalysts are more complex and comprise less defined active sites, but they are based on more earth-abundant metals and are less susceptible to leaching. Therefore, the surface study and design of more active and selective oxide catalysts are important matters in light of the green transition. In this regard, oxides of the spinel type proved to be outstanding catalysts in liquid-phase aerobic oxidations [3].

Experimental/methodology. A library of nanocrystalline spinels based on Mn, Fe, Co, Ni, Cu and Zn was prepared using the combustion method followed by calcination. The obtained solids were characterised by XRD, FT-IR, SEM-EDX, N_2-physisorption, and XPS. The catalysts were tested in the liquid-phase oxidation of 2-propanol and -butanol in a flow reactor, and the collected liquid and gas samples were analysed by GC-FID.



Results and discussion. Every spinel with a different elemental composition produces a different type of combustion, which is reflected in the different morphology and phase composition of the solids. While the as-synthesised Mn, Co and Ni ferrites are pure, the rest of the combinations required calcination, each with a different temperature, atmosphere and cooling. The temperature stability of each material was tested to assess the suitability of different pretreatments, as well as the crystal growth during those. The catalysts were tested in a flow reactor, in the presence of water and O_2, to study the effect of the catalyst composition on the activity and selectivity, together with the impact of the presence of a normal-vs-inverse spinel configuration and a cubic-vs-tetragonal structure. Finally, the stability of the catalyst to water and to the reaction conditions was also assessed.

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Strategy to enhance metallic dispersion via regulation of metal-support interactions on the example of Ni/Al_2O_3 catalyst

E. E. Taş[1,2], B. S. Çağlayan[2,3], A. E. Aksoylu[1,2*]

[1]*Department of Chemical Engineering, Boğaziçi University, Bebek, Istanbul 34342, Turkey*
[2] *SNG&HydTech Lab, Science and Technology Building, Boğaziçi University, Kandilli, Istanbul 34684, Turkey*
[3] *Advanced Technologies R&D Center, Boğaziçi University, Bebek, Istanbul 34342, Turkey*
[*]*aksoylu@boun.edu.tr*

Keywords: Dispersion enhancement, Catalytic activity, Stability of catalyst, Complexation, Adsorption

Introduction. High catalytic activity, desired selectivity and long-term stability are key features associated with the effective catalyst in the context of heterogeneous catalysis. For a targeted reaction, these features strongly depend on the reaction conditions and multi-way interactions between reactants, active sites and support material. Therefore, active sites on catalyst must be designed and optimized to increase catalytic performance. In this study, a synthesis strategy for dry impregnation (DI) method is proposed to enhance active metal dispersion and stability on support material via Ni/Al_2O_3 catalyst example.

Experimental/methodology. Effect of support type, precursor compound, impregnating solution and calcination temperature were analyzed to enhance metal dispersion level on Ni/Al_2O_3 catalyst by DI method. Point of zero charge (PZC) values of supports were measured and used to predict the pH at maximum adsorption by a simplified physical adsorption model [1]. Surface of impregnated supports were analyzed by Raman spectroscopy. Three different calcination temperatures (500, 700, 900°C) were applied. H_2 chemisorption was used to determine Ni dispersion levels. Selected samples and supports were characterized by their BET surface area, pore volume, pore size distribution, XRD and Raman spectroscopy.

Results and discussion. Since nickel is a low oxidation state metal and can be accommodated in Al_2O_3 spinel by absorption on surface, theoretical adsorption model is not suitable for Ni^{2+} [2]. However, complexes of nickel show high stability and are mainly adsorbed on support surface that makes possible to apply physical adsorption model. Theoretical equilibrium calculations and UV–vis spectroscopy evidenced the formation of targeted Ni complexes (EDTA, NTA, citric acid, ammonia) in impregnating solutions. Nickel-ammonia complexes have lower dispersion levels from theoretical calculations because of the $Ni(OH)_{2(s)}$ formation at high pH levels. As shown in Figure 1, catalysts prepared by using Ni-EDTA complex shows higher dispersion at 900°C while citric acid and NTA addition results with significantly higher dispersion levels at lower calcination temperatures.

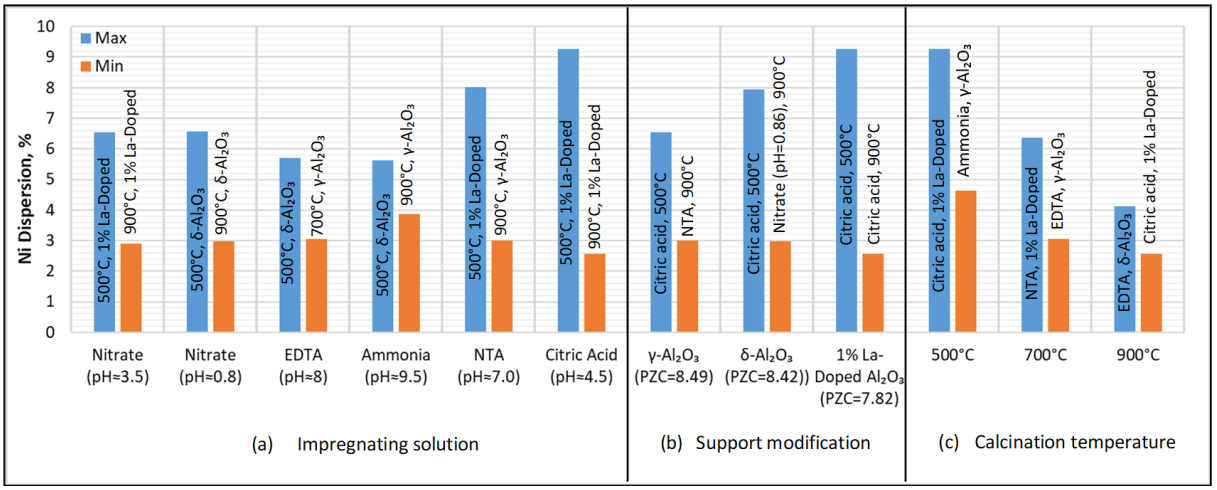

Figure 1. Maximum and minimum dispersion levels of manufactured catalysts.

Acknowledgments

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Diastereoselective Synthesis of Novel Phosphine-Phosphoramidite Ligands and their Performance in Asymmetric Catalysis

Simon Teeuwen[1], Giancarlo Franciò[1*], Walter Leitner[1,2]

[1]*RWTH Aachen University, Institute for Technical and Macromolecular Chemistry, Aachen, Germany*
[2]*Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany*
[*]*francio@itmc.rwth-aachen.de*

Keywords: asymmetric synthesis, asymmetric catalysis, hydroformylation, hydrogenation

Introduction. From pharmaceuticals and agrochemicals, over flavors and fragrances to material sciences, asymmetric synthesis plays a crucial role for accessing a plethora of chiral organic molecules.[1] We endeavor to enlarge the catalyst availability through easily accessible and effective chiral ligands. Herein, we present a route to diastereoselectively synthesize novel phosphine-phosphoramidite ligands. Those ligands are then used in two of the largest homogeneously catalyzed reactions, i.e. the Rh-catalyzed asymmetric hydrogenation (AH) and hydroformylation (AHF).[2]

Experimental/methodology. Starting from simple 2-(diarylphosphino)benzaldehyde, a first stereocenter is introduced into the ligand structure by a facile condensation reaction with a chiral amine (see Figure 1). The presence of a stereocenter acting as directing group allows the diastereoselective functionalization of the imine upon addition of an organometallic reagent and the generation of a second stereocenter in a controlled manner. This strategy permits to largely overcome the challenging separation of diastereomers formed in equimolar amounts during synthesis, as it was the case for the related Quinaphos ligands.[3] Addition of an organometallic reagent and introduction of the desired phosphoramidite moiety could be conveniently done in a one-pot synthesis for some derivatives. Alternatively, the phosphine-amine (or the corresponding hydrochloride salt) can be isolated and then functionalized with the phosphoramidite moiety.

Results and discussion. Through this methodology, a mini library of chiral imines and phosphine-phosphoramidite ligands have been synthesized varying both R* and R' and achieving diastereoselectivities of up to 99 % during imine functionalization. The phosphine-phosphoramidite ligands have then been used in asymmetric hydrogenation, as well as asymmetric hydroformylation of benchmark substrates. The results obtained will be presented.

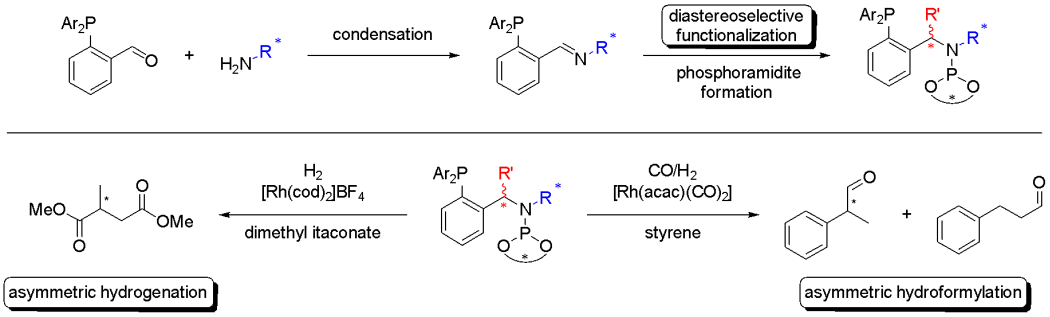

Figure 1: Synthesis of chiral phosphine-phosphoramidite ligands (top) and their application in asymmetric catalysis (bottom).

Acknowledgments

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Highpressure pulse experiments and cofeeding of ethylene: Insight into the active sites of a prussian blue analoguederived Mn-Co catalyst in the CO hydrogenation to higher alcohols

P. Telaar[1], P. Schwiderowski[1], P. Diehl[1], M. Muhler[1]

[1]*Laboratory of Industrial Chemistry, Ruhr University Bochum, Bochum, Germany*
[*]*Corresponding author: muhler@techem.rub*

Keywords: higher alcohol synthesis, prussian blue analogues, carbonylation, hydroformylation, steadystate kinetics, highpressure pulse experiments

The heterogenously catalyzed hydrogenation of carbon monoxide to higher alcohols has attracted substantial attention in the last decades due to the possibility of decreasing the dependence on fossil fuels. Therefore, the application of climateneutral fuels obtained by higher alcohol synthesis (HAS), shown in Equation 1, is an important factor to mitigate the global CO_2 emissions in the next decades.[1]

$$n\,CO + 2n\,H_2 \rightarrow C_nH_{2n+1}OH + (n-1)\,H_2O \; n\,CO + 2n\,H_2 \rightarrow C_nH_{2n+1}OH + (n-1)\,H_2O \quad (1)$$

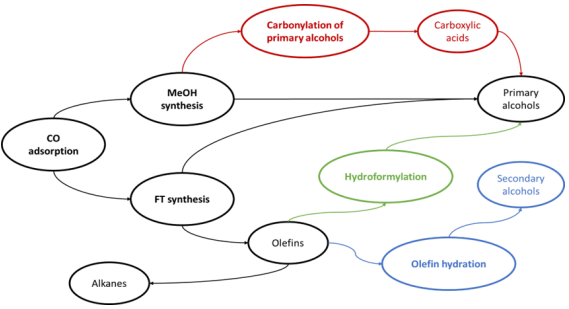

Figure 1. Proposed schematic reaction network for the HAS using PBA based catalysts.

This work further investigated the reaction network, shown in Figure 1, of a Cobased catalyst derived from a prussian blue analogue (PBA).[2-3] During our previous work, the pyrolysisbased synthesis of the catalysts was further improved resulting in a Cobased catalyst promoted with Mn^0, but no longer with K.[3] Here, the most promising approach was the implementation of a washing step, leading to increased CO conversion and a higher total oxygenate selectivity.[3] Consequently, the steadystate kinetics as well as transient kinetics of this $Mn_{1.0}Co_{10.6}$ catalyst were further investigated in this study. Highpressure pulse experiments with MeOH and NH_3 were performed to gain deeper insight into the interplay of the carbonylation of primary alcohols, reductive hydroformylation of olefines as well as the olefin hydration. In addition to the established variation of reaction temperature, pressure, residence time and partial pressures of CO and H_2, a cofeeding experiment was performed. While maintaining a CO:H_2 ratio of 1, ethylene was constantly added to the feed gas to investigate the influence of the hydroformylation reaction pathway. The performed kinetic study gave deeper insight into the interplay of presumably two active sites present in Cobased catalysts derived from PBAs. The cofeeding experiment showed that the increased partial pressure of ethylene resulted in an increased formation of 1PrOH, while no increased formation rate of the longerchain primary alcohols was observed, suggesting that in addition to the *in situ* formed Co_2CCo interface embedded in the highly functionalized carbon matrix, another active site for the oxygenate formation is present. Based on recent studies,[4] this active site can be assumed to be an *in situ* formed Co carbonyl hydride complex. The necessary stability is ascribed to the presence of the nitrogen and oxygenfunctionalized carbon matrix, resulting in an efficient anchoring of this labile complex. However, further studies are needed to fully understand the nature of the active sites using PBAbased catalysts. *In situ* DRIFTS and *in situ* XPS are currently performed to investigate the surface transformations taking place under reaction conditions.

Acknowledgments

The research project was funded by the German Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF, Verbundvorhaben Carbon2Chem®, L4: C_{2+}-Alkohole, C_{2+}Olefine, synthetische Kraftstoffkomponenten, FKZ: 03EW0008C).

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Investigating the activity and stability of Pt/Si-doped TiO_2 for total propane oxidation

Max Tigwell[1], Mark Douthwaite[1], Liam Bailey[1], Louise R. Smith, Nicholas F. Dummer, David J. Morgan[1], Stuart H. Taylor[1] and Graham J. Hutchings[1].

[1]*Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis, FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, U.K*
Correspondence to: TigwellMJ@cardiff.ac.uk

Introduction

The doping of supported heterogeneous catalysts can significantly affect their physicochemical properties which, in turn, can dramatically influence their catalytic performance.[1] Herein, a series of Si-doped TiO_2 metal oxide materials were synthesized using a sol-gel technique and used as supports for Pt nanoparticles, which were deposited by chemical vapour impregnation (CVI). We demonstrate that the incorporation of Si into the lattice of the TiO_2 support can drastically influence the activity and stability of the supported Pt particles in the total oxidation of propane under wet, industrially relevant conditions.

Experimental/methodology.

Si_x-TiO_2 (x = 0 – 16 *wt.*%) materials were prepared by a sol-gel method and used as catalysts and supports for Pt nanoparticles. For the latter, 1 wt.% of Pt was deposited by chemical vapour impregnation (CVI). Phase purity and crystallinity measurements were determined by X-ray diffraction. Support surface area and porosity measurements were determined by N_2 physisorption. Acidity measurements were acquired from NH_3 temperature programmed desorption (TPD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments with pyridine. Data relating to the Pt particle size and dispersion, in fresh and used catalysts, was acquired from CO chemisorption and transmission electron microscopy (TEM) experiments. The catalytic performance of the materials prepared in this study were acquired from experiments conducted in a continuous flow fixed bed reactor, under wet and dry conditions. A premixed cylinder of 1000 ppm propane in 10% O_2 in N_2 was used, a gas hourly space velocity (GHSV) of 50,000 h^{-1}.

Table 1. Temperature of propane conversion at T_x x = conversion, Pt dispersion based on CO chemisorption, BET surface area measurements.

Catalyst	T_{20}	T_{50}	Dispersion (%)	BET Surface Area (m^2/g)
Pt/TiO_2	209	236	33	68
$Pt/Si\text{-}TiO_2$ (1%)	217	243	90	149
$Pt/Si\text{-}TiO_2$ (2%)	210	240	75	222
$Pt/Si\text{-}TiO_2$ (4%)	204	228	59	235
$Pt/Si\text{-}TiO_2$ (8%)	183	220	46	255
$Pt/Si\text{-}TiO_2$ (16%)	237	291	6	342
Pt/SiO_2	213	250	6	798

Results and discussion.

The incorporation of Si into the lattice of the TiO_2 supported Pt catalysts had a profound effect on their catalytic activity towards total propane oxidation. Low loadings of Si promoted Pt dispersion, which was confirmed by TEM and CO chemisorption. On the contrary, higher Si loadings increased Pt dispersion and was collectively, confirmed as a key activity descriptor for the reaction (**Table 1**). Importantly, the incorporation of Si was also found to influence the stability of the $Pt/Si\text{-}TiO_2$ catalysts and influenced their resistance to H_2O. Ammonia TPD and In-situ DRIFTS experiments using pyridine, CO and propane as probe molecules were employed to uncover important features relating to the reaction mechanism, which confirmed that the C-H bond activation was rate determining.

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Garnet-Type Materials as Multifunctional Catalysts in Challenging Applications of CCU

J. Titus[1], C. Fritsch[2], T. Roussière[2], C. Lizandara-Pueyo[2], R. Müller[2], R. Gläser[1], S. A. Schunk[1,2*]

[1]*Institute of Chemical Technology, Universität Leipzig, Leipzig, Germany*
[2]*hte GmbH, Kurpfalzring 104, Heidelberg, Germany*
[*]*Stephan.Schunk@hte-company.de*

Keywords: Yttrium aluminium garnets, exsolution, dry reforming of methane

Introduction. Synthesis gas (syngas) can be produced by several industrial processes, e.g., steam reforming of hydrocarbons or partial oxidation. An alternative is the highly endothermic dry reforming (DRM) in which an equimolar syngas product in obtained [1]. Ni and Co are promissing active metals in DRM catalysts, nevertheless, deactivation caused by sintering needs to be prevented. Hence, complex oxide structures, e.g., spinells or perovskites were investigated [2]. Here, we report the synthesis of complex mixed-oxides by two routes, from which the active metal can be extracted via exsulution. The phase pure Ni- and Co-substituted Y-Al-garnets (YAG) as DRM catalysts.

Experimental/methodology. YAG catalysts were prepared via the conventional Pechini and polymer-analogue Flocculant route acording to [3]. Fresh and spend catalysts were characterized by e.g. XRF, N_2 sorption and TPR. By means of XRD and TEM-EDX, the phase purity of the obtained garnets and the effect of activation was studied. The catalytic activity was investigated in the DRM for 15 h time on-stream (TOS). After activation (1 h, 10 vol.-% H_2 in Ar at 1123 K), catalytic studies at ambient pressure under conditions of $n(CH_4)/n(CO_2) = 1$, T = 1023-1123 K and GHSV = 6000 h^{-1} were conducted.

Results and discussion. Phase pure Ni- and Co-substituted YAGs were synthesized. Here the applied route had a significant influence on, e.g., crystalinity and catalytic activity. The ocurance of crystalline side phases was observed not only depending on the synthesis route, but also on molar composition and calcination temperature. In general, applying the Flocculant route led to an increased phase purity of YAGs as well as an enhanced porosity compared to the conventional Peccini based catalysts. Applied in DRM, Ni-based YAGs were found to be more active (Fig. 1 right) and less prone to carbon depositions then their Co-containing analogues. Ni^0 sites were found to be the active phase since reduction prior to DRM caused an exsolution of Ni from the crystal structure. It should be noted, that the activity of Co-YAGs was found to be higher, if no activation in H_2 was conducted. Hence, oxidic cobalt seems to play a significant role regarding catalytic activity and coke resistance.

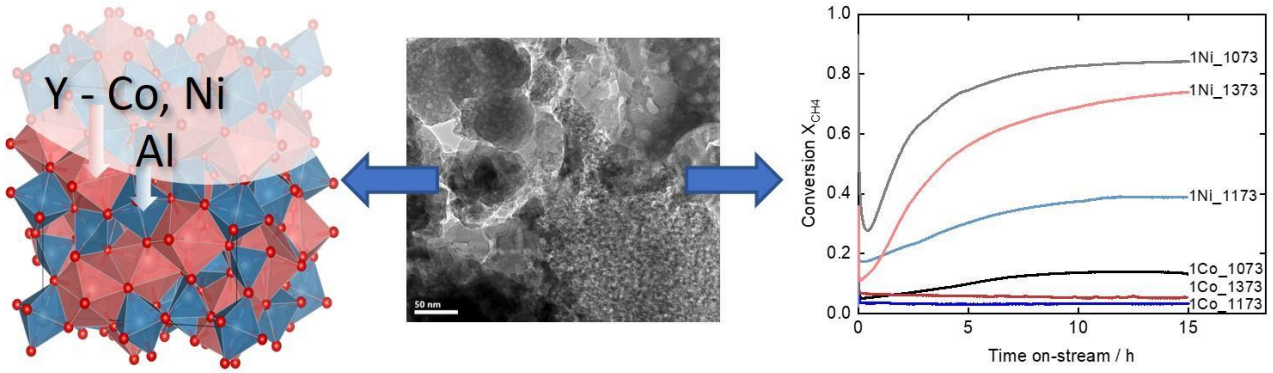

Figure 1. Graphical abstract displaying the YAG structure (left), a TEM image of phase pure YAG (middle) and the activity in DRM with the conversion X_{CH4} versus time on-stream for 1 mol-% Ni- and Co-substituted YAGs calcined at different temperatures (right).

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Platinum nanoparticles supported on polybenzimidazole nanofiber mats: application to VOC oxidation

P. Topka[1*], K. Soukup[1], J. Kupčík[1], J. Balabánová[1], M. Koštejn[1], O. Šolcová[1]

[1] *Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, Praha, Czech Republic*
[*] *topka@icpf.cas.cz*

Introduction

Structured catalysts with high porosity and low pressure drop are particularly suitable for industrial processes carried out at high space velocities. One of these processes is catalytic total oxidation of volatile organic compounds, which is economically feasible and environmentally friendly way of emission abatement. Noble metal catalysts are typically preferred due to high activity and stability. Designing catalysts with low amount of active phase is important for industrial applications [1]. Herein we report the preparation of thermally stable electrospun mat, which can be used as a support for platinum catalysts.

Experimental

Electrospun polybenzimidazole support was impregnated with platinum(II) acetylacetonate.

Results and discussion

The morphology of the support allowed to prepare catalysts with high porosity and low mass transfer limitations. Moreover, by tuning the preparation conditions, it was possible to obtain catalysts with different Pt loading and particle size. The Pt active sites were deposited on the surface of nanofibers (Fig. 1) and were readily accessible to the reactants. As a result, the catalyst containing only 0.08 wt.% of Pt was able to reach a high conversion (90 %) of model VOCs (ethanol, acetone, toluene) at moderate temperatures (229 °C, 271 °C, and 334 °C, respectively).

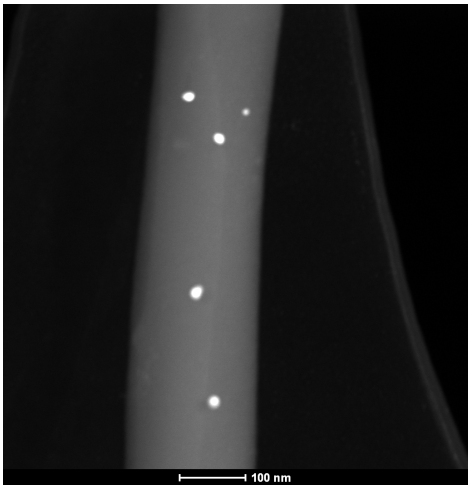

Fig. 1. STEM image of Pt nanoparticles supported on polybenzimidazole nanofiber mat.

Furthermore, we have shown that the TOF depends on the size and type of Pt nanoparticles. The catalysts with Pt particle sizes 1.5 nm and 26 nm exhibited lower catalytic activity than that with Pt particle size of 12 nm. The catalysts with Pt particle size 1.5 nm and 12 nm were prepared by equilibrium adsorption and the higher catalytic activity of the latter catalyst can be explained by the decrease of the Pt–O bond strength with the enlargement of the Pt particle size, which led to more reactive adsorbed oxygen on Pt sites. On the other hand, the catalyst with Pt particle size 26 nm was prepared by solvent evaporation method and contained polycrystalline platinum. Thus, although the Pt particle size determined by TEM was 26 nm, the size of single coherent domains was lower, which correlated with the lower catalytic activity of this catalyst.

Acknowledgement

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3D-printed carbon catalysts for oxalic acid ozonation

José R.M. Barbosa[1,2*], Maria João Regufe[1,2], João Restivo[1,2], Carla A. Orge[1,2], Alexandre F.P. Ferreira[1,2], Manuel F. R. Pereira[1,2], Ana Mafalda Ribeiro[1,2], Olívia S. G. P. Soares[1,2]

[1]*Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE–LCM), Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, 4200-465, Porto, Portugal*

[2]*ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

[*]*Corresponding Author: jrbarbosa@fe.up.pt*

Keywords: Additive manufacturing, carbon materials, heterogeneous catalysis, ozonation

Introduction. Additive manufacturing, also known as 3D printing, in catalysis has been the target of several studies because it allows to transform powder catalysts into 3D structures that are adaptable for different operation conditions, easy to manipulate and optimize the processes of mass transfer [1]. Catalysts based on carbon materials, such as multi walled carbon nanotubes (MWCNT) and activated carbon (AC) have been studied to reduce different types of environmental pollutants in liquid and gas phases due to their excellent textural and mechanical properties [2-4]. Their application is generally studied in suspensions in the effluents to be treated and/or fixed beds, making the introduction in large-scale processes difficult. In this study, macro structured catalysts of MWCNT and AC through the direct writing technique were developed to be applied in the ozonation of oxalic acid in the liquid phase.

Experimental/methodology. The macro-structured catalysts were developed by direct writing printing. Sodium carboxymethyl cellulose (CMC) was used as a binder to prepare the inks, and deionized water was used as a solvent. Briefly, the carbon materials were mixed with CMC using ball milling equipment (at low frequency). Then the resulting mixture was wetted drop by drop and stirred until a workable rheology for printing was obtained. The mixture was immediately inserted into a syringe, and the printing process was carried out by applying controlled pressure. Macrostructures of AC and MWCNT with 20 wt.% of CMC (AC_20CMC and MWCNT_20CMC, respectively), and thermal treated MWCNT_20CMC at 250 and 500 ^{0}C (MWCNT_20CMC_250 and MWCNT_20CMC_500, respectively) were prepared and tested in oxalic acid ozonation in a semi-batch system.

Results and discussion. Stable structures were obtained for all the prepared inks demonstrating that CMC is a viable binder for this purpose. Moreover, the manufactured thin MWCNT structures exhibited high flexibility, whilst the AC structures collapsed when some light pressure was applied. Thermogravimetric analysis confirmed the two selected temperatures for CMC degradation, and at 500 ^{0}C, almost all CMC was degraded. In addition, the textural properties were determined, and S_{BET} of MWCNT_20CMC (136 m^2 g^{-1}) increased with the temperature of the applied thermal treatments. The kinetics were determined at 30 min of oxalic acid ozonation reaction, and the catalyst MWCNT_20CMC_250 obtained the most promising results, followed by MWCNT_20CMC and lastly, MWCNT_20CMC_500. It was evidenced that 250 ^{0}C is the optimal temperature to improve the catalytic properties, likely due to an optimal compromise between morphology and binder degradation. The AC structures crumbled into powder during the reaction, which is not feasible for the intended application of this work.

Acknowledgments

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Porous Tin-Organic Frameworks as a Selective Epimerization Catalysts for the Synthesis of Rare Monosaccharides

V. Toussaint[1*], T. Röper[1], L. Pavlis , I. Delidovich[1].

[1]*Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, Vienna, Autria.*
[*]*valerie.toussaint@tuwien.ac.at*

Keywords: Porous organic frameworks, epimerization, isomerization, saccharides, aqueous solution.

Nowadays, the interest in biomass valorization in technological areas such as chemical, fuel and food industry is rapidly increasing. In this regard, the conversion of abundant into rare monosaccharides with significant application potential in medical and pharmaceutical industry is of great interest. [1]

Element-organic frameworks are a young class of nanoporous inorganic-organic hybrid materials. Recently, catalytic activity for epimerization of monosaccharides of Lewis acidic porous tin-organic frameworks (Sn-OF) was uncovered.[2a]

A few Sn-OFs were synthesized *via* corresponding lithium intermediates as summarized in Figure 1a starting from the linkers shown in Fig. 2b. The synthesized materials were characterized by elemental analysis, low-temperature N_2 physysorption, ^{1}H, ^{13}C, and ^{119}Sn MAS NMR, EXAFS, XANES, IR spectroscopy, and SEM. We currently work on elucidating structure performance relations of the Sn-OFs.

High reaction rates were achieved for epimerization of monosaccharides, i.e. glucose and xylose, whereas transformation rate of lactose dissacharides was two orders of magnitude lower. We explain this result by inaccessibility of the active sites located in micropores.The Sn-OFs were applied to convert readiliy available monosaccharides into rare and expensive products. The epimerizations of D-glucose to D-mannose, L-ribose to L-arabinose, D-xylose to D-lyxose, D-galactose to D-talose, and L-rhamnose to L-quinovose were explored. The conversion for Sn-OF-1 was in the range of 12-36% with a selectivity for the epimerization product of 77-90% at 100 °C after 1.5 h (Figure 1c). [2] The rare monosaccharides are highly demanded as precursors in pharmaceutical and food industries.[4]

Development of an efficient product recovery presents a key element of process design. We work on product separation *via* adsorption, focusing on elaborating materials with high affinity towards the desired products. For instance, D-mannose is selectively adsorbed on CaY zeolite from D-glucose-D-mannose, with separation factor up to 4.2, owing to complexation of the eq-ax-eq motive of D-mannose with Ca^{2+} ions.

The results of this project will provide a knowledge-driven basis for manufacture of rare saccharides.

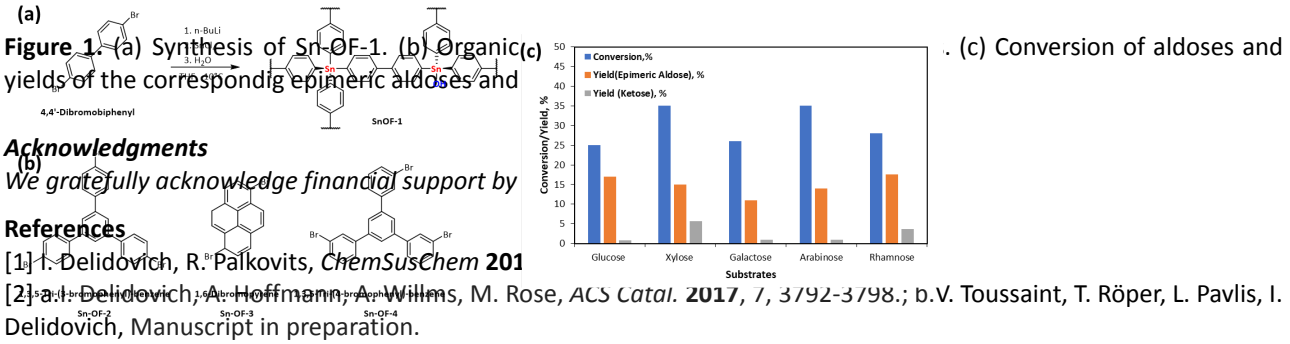

Figure 1. (a) Synthesis of Sn-OF-1. (b) Organic . (c) Conversion of aldoses and yields of the correspondig epimeric aldoses and

Acknowledgments

We gratefully acknowledge financial support by

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Electric Field-Enhanced Low-Temperature Ammonia Decomposition over $RuCeO_2$ Nanoclusters

M.L.T. Triviño[1], Cheol Ung Lee[1], Y. Sekine[2], J. G. Seo[1*]

[1]*Department of Chemical Engineering, Hanyang University, Seoul, South Korea*
[2]*Department of Applied Chemistry, Waseda University, Tokyo, Japan*
[*]*E-mail: jgseo@hanyang.ac.kr*

Keywords: ammonia decomposition, electric field, ruthenium

Introduction. Ammonia is regarded as a promising hydrogen carrier for on-site use as it has high H_2 content (17.6 wt%) and can be easily decomposed into H_2 and N_2 without liberating CO_x and other impurities.[1] However, NH_3 decomposition requires high temperatures (> 500°C) even in the presence of catalysts. Ruthenium is by far the only catalyst that can give significant conversions at temperatures below 500°C, but full conversions at lower temperatures are still unattainable.[2] On the other hand, the application of an external electric field (EF) has been reported to lower temperatures and enhance catalyst activity for several reactions. In this study, we present the synthesis of Ru nanoclusters on CeO_2 via a facile support precipitation and impregnation route and investigated the effect of applying an EF on catalyst performance towards NH_3 decomposition.

Experimental/methodology. The $RuCeO_2$ catalysts were synthesized via a modified oxalate precipitation and impregnation route.[3] Catalytic tests were carried out on a fixed bed reactor equipped with stainless steel electrodes that are connected to a DC power supply. Effluent gases were then analyzed by GC-TCD.

Results and discussion. Catalysts with Ru loadings of 1, 2.5, and 4 wt% were synthesized and characterized, from which it was found that the catalysts possess high surface areas, small particle sizes, and good dispersion. The catalysts were then evaluated for NH_3 decomposition at GHSVs of 30,000 and 3,000 $mL_{NH3}/gcath$ with and without EF. As seen from Figure 1, significant increase in conversions at all temperatures were obtained upon applying an EF of 5mA current. Interestingly, considerable conversions were obtained at low temperatures in the presence of EF. Notably, NH_3 conversions reached a value of > 60% at T = 450°C and 30,000 $mL_{NH3}/g_{cat}h$, and > 90% at T=350°C and 3,000 $mL_{NH3}/g_{cat}h$, which are much higher than previous reports at the same temperatures. Moreover, catalyst conversion further improves with decreasing GHSVs, allowing the $4RuCeO_2$ catalyst to exceed equilibrium values at T = 250°C.

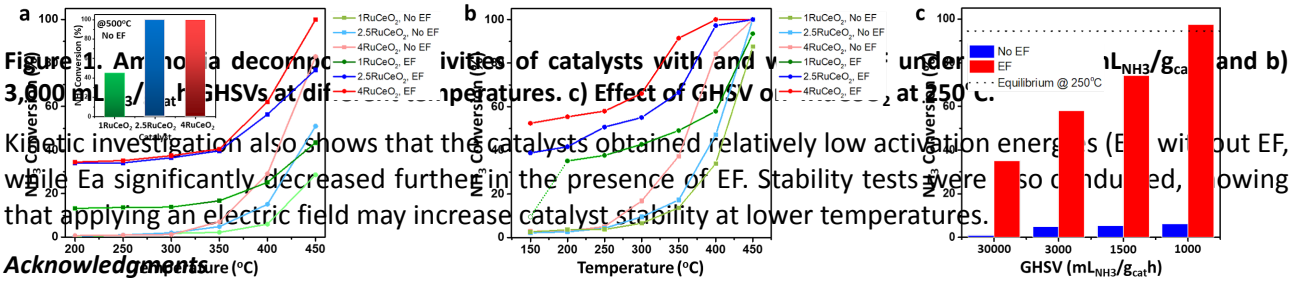

Figure 1. Ammonia decomposition activities of catalysts with and without EF under mL_{NH3}/g_{cat} and b) 3,000 $mL_{NH3}/g_{cat}h$ GHSVs at different temperatures. c) Effect of GHSV on NH_3 conversion at 250°C.

Kinetic investigation also shows that the catalysts obtained relatively low activation energies (Ea without EF, while Ea significantly decreased further in the presence of EF. Stability tests were also conducted, showing that applying an electric field may increase catalyst stability at lower temperatures.

Acknowledgements

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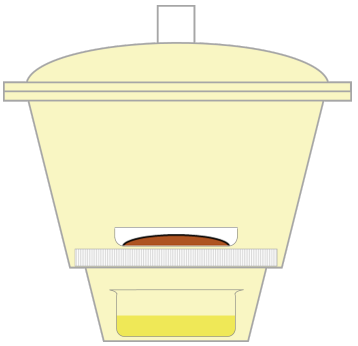
Self-catalyzed hydrophobing by VOC exposure of mixed-metal oxide catalyst for CO oxidation in humid conditions

N. Unglaube[1*], J. Grothe[1], S. Kaskel[1]

[1]*TU Dresden, Dresden, Germany*
[*]*niklas.unglaube@tu-dresden.de*

Keywords: CO oxidation, non-noble metal, moisture resistance, surface modificaton

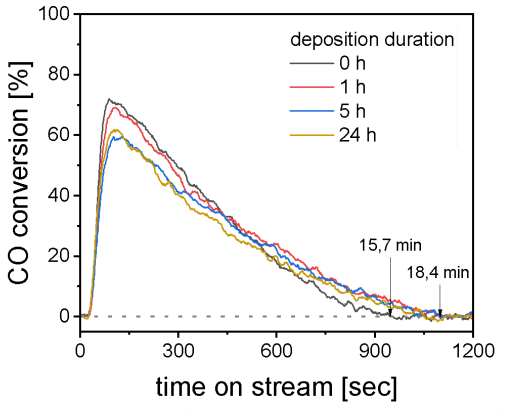
Introduction. Oxidation catalysts for user-friendly air purification have the special requirement to be applicable at ambient conditions. This is especially challenging for catalytic materials in gas-mask applications because of highly humid conditions. A common catalyst for CO gas masks is e.g. the non-noble mixed metal oxide Carulite®, which suffers from deactivation from environment and breath humidity resulting in a decreased durability.[1] To improve the moisture resistance of catalysts various approaches use the hydrophobicity of carbon materials to prevent the adsorption of water on the catalysts surface.[1–3] The carbon modifications are carried out by pyrolysis of carbon precursors or attachment of carbon nanofibers. Here, we demonstrate the non-destructive polymerization of hydrophobic aromatics on the catalysts surface as new method for improved moisture resistance.



Schematic depiction of the VOC saturated dissicator

Experimental/methodology. The modification was carried out using Carulite® in a dissicator under saturated volatile organic compound (VOC) atmosphere for different durations. To remove unpolymerized VOC, the catalyst was dried over night at 150 °C. For screening the hydrophobicity and moisture-resistant catalytic activity, InfraSORP techniques were used to resolve the thermal response of heat of reaction and adsorption. Furthermore, 100 mg of the moisture resistant catalyst was tranfered into a reactor tube and activated at 120 °C for 30 min in synthetic air. The CO conversion was tested with 0.7 % CO in a 60 mL min^{-1} synthetic air stream with 75 % relative humidity (r.h.). To determine the catalytic lifetime, the CO and CO_2 concentrations were measured and evaluated. H_2O, N_2-physisorption and elemental analysis were carried our for every sample while the most promising samples underwent closer characterization.

Results and discussion. First experiments revealed a simple and reproducible method to create humidity resistance at room temperature. The modified catalyst exhibits a smaller water uptake while it highlights a prolonged CO oxidation lifetime at 75 % r.h. and room temperature. The deposited carbon by CHNS analysis seems to be of no significant amount while TEM images could not reveal the morphology of deposited coke, yet. Further investigations are focussed on the The applied modifications on the catalyst and the influence of different VOCs.



CO removal over TOS at 75 % r.h. with commercial and modified Carulite®

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Alternative approach to Zeolite/Carbon composites synthesis with enhanced CO_2 adsorption properties

F. Valentini[1], P. Tawachkultanadilok[2], J. Wittayakun[2], K. Föttinger[1*]

[1]*Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria*
[2]*School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, Thailand, 30000*
[*]*karin.foettinger@tuwien.ac.at*

Keywords: Zeolite, NaY, carbon, composite, microcrystals, nanocrystals, CO_2 adsorption.

Introduction. The continuous expansion of civil society, with the change in lifestiles and resources use, leads necessarily to an higher impact of the industrial facilities on the surrounding environments. As it is well known, nowadays CO_2 emissions are still one of the major effects of industrial pollution. The aim of this work is to show that composites zeolite/carbon materials could act as useful CO_2 adsorbants in the field of environmental preservation. Examples of such materials are widely used for the most diverse application, ranging from stabilizers for electrochemical batteries to enhance in thermal energy storage, or also for treatment of industrial waste water [1]. Usually, the approach that is used to obtain such composites is to disperse a precise amount of carbon from different sources (palm oil, coal, rice hulls, …) directly on the zeolite support.

Experimental/methodolgy. Here we propose a direct synthesis of the NaY zeolite with 3 different carbon sources (activated carbon - AC, carbon black - CB and graphite - GP) by hydrothermal method aimed at obtaining microcrystal-sized and nanocrystal-sized samples. In general, all ours samples have been characterized by SEM, FT-IR, XRD, TGA, N_2-physisorption and TPD techniques.

Results and discussion. Similar approaches already showed enhanced CO_2 adsorption properties in the case of carbon black composite with a zeolite 13X [2], while carbon black itself usually needs to be activated by surface modification (or coating) with an adequate CO_2 adsorbant [3]. This is consistent with ours result, as the pure carbon phases that have been used for the composites didn't show any CO_2 adsorption property at the investigated temperature before being coupled with the NaY zeolite. After confirming the Faujasite crystalline phase of each composite by XRD, SEM pictures showed an higher average diameter of the NaY-AC with respect to the other samples. However, TPD measurements of this sample exhibits amounts of adsorbed CO_2 that are quite comparable to the pure NaY zeolite, while in the case of the other composites this increase showing higher CO_2 adsorption performances for the NaY-CB and finally the best for the NaY-GP composite.



Acknowledgments
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Switching selectivity in the oxidative dehydrogenation of cyclohexene by atomic-precision control of catalyst composition

S. Valtera[1], J. Jašík[1], M. Vaidulych[1], J. E. Olszówka[1], M. Bunian[2], Y. Lei[2], A. Halder[3], H. Tarábková[4], M. Zlámalová[4], M. Jindra[4,5], L. Kavan[4], O. Frank[4], S. Bartling[6], Š. Vajda[1]

[1]*Department of Nanocatalysis, J. Heyrovský Institute of Physical Chemistry v.v.i., Czech Academy of Sciences, Prague, Czech Republic*

[2]*University of Alabama in Huntsville, United States of America*

[3]*Materials Science Division, Argonne National Laboratory, Lemont, United States of America*

[4]*Department of Electrochemical Materials, J. Heyrovský Institute of Physical Chemistry v.v.i., Czech Academy of Sciences, Prague, Czech Republic*

[5]*Department of Physical Chemistry, University of Chemistry and Technology in Prague, Prague, Czech Republic*

[6]*Leibniz Institute for Catalysis (LIKAT), Rostock, Germany*

stanislav.valtera@jh-inst.cas.cz

Keywords: nanoalloys, size selected clusters, subnanometer clusters, oxidative dehydrogenation

Introduction. Supported single atoms and subnanometer clusters of transition metals proved to be promising catalysts in various reactions, including dehydrogenation processes that belong to the most important ones in the chemical industry for the synthesis of olefins and aromatic intermediates for the production of fine chemicals or polymers. With their high surface-to-volume atomic ratio, and most of the atoms being undercoordinated and therefore very reactive, subnanometer size clusters open new avenues for the design of new classes of high-performance catalysts with their activity and selectivity controllable at the atomic level [1].

Experimental/methodology. The synthesis of atomically precise $Cu_{4-n}Pd_n$ ($0 \leq n \leq 4$) clusters of select atomic compositions was performed in molecular beams in the gas phase and clusters of single size and composition deposited on commercially available ultrananocrystaline diamond (UNCD) support as well as on silicon wafers coated with thin layers of ZrO_2 and TiO_2 using atomic layer deposition. Catalytic tests were performed in a custom reactor under a continuous flow of a reactant mixture containing 0.3 % cyclohexene and 0.3 % oxygen seeded in helium at a pressure of 1.1 bar, in a temperature range from 25 °C to 400 °C and products analyzed on a mass spectrometer.

Results and discussion. The results show that by altering the composition of the cluster in an atom-by-atom fashion in synergy with the effect of support leads to significant changes in catalytic reactivity and selectivity, up to switching the selectivity between the main dehydrogenation products benzene and cyclohexadiene, and that as much to totally suppressed combustion to CO_2. For instance, to just illustrate the size, composition, and support effects, titania-supported monometallic Cu and bimetallic CuPd tetramers exhibit 100 % selectivity towards benzene. UNCD-supported Pd_4 clusters are highly active without any combustion to CO_2 despite the known potency of Pd as a combustion catalyst. Central results are shown in Figure 1, which shows a gradual change in the selectivity of zirconia-supported tetramers when changing the atomic ratio between Pd and Cu in an atom-by-atom fashion, ultimately switching selectivity from benzene to cyclohexadiene on the way going from Pd_4 to Cu_4.

Figure 1: Selectivity for benzene, cyclohexadiene and CO_2 at 400 °C for all tetramers $Cu_{4-n}Pd_n$ on ZrO_2.

Acknowledgments

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Supported Metal-Catalyzed Polymer Modification via Hydrogenation and Hydrodechlorination reactions

V. Varela-Izquierdo[1], G. Mencía[1], B. Chaudret[1,*]

[1]*LPCNO, Laboratoire de Physique et Chimie des Nano-Objets, INSA, CNRS, UPS, Université de Toulouse, 135, Avenue de Rangueil, F-31077 Toulouse, France*

varelaiz@insa-toulouse.fr

Keywords: hydrogenation, hydrodechlorination, polymers, ruthenium, nickel, palladium.

Introduction. Polymeric structure modification is a well-known methodology providing novel materials with tailored physical properties, thereby increasing the application range of the original polymer.[1] In particular, aromatic polymer hydrogenation catalyzed by Pd and Pt catalysts has been widely used to alter the polymeric chain.[2] On the other hand, Ni and Pd catalyst are commonly used in hydrodechlorination reactions under hydrogen atmosphere for small organic molecule modification[3]. However, in the case of polymers, these catalysts remain unexplored and radical-based reactions are preferred[4]. Those two strategies were applied to modify commercial polymers in the work herein presented.

Experimental/methodology. Supported Ru, Ni & Pd NPs (5-10 wt%, figure 1) were prepared by thermal decomposition of Ru(COD)(COT), $Ni(COD)_2$ or $Pd_2(DBA)_3$ in the presence of different supports (Carbon, Mesoporous Carbon, SiRAlOx, TiO_2). The synthesis was carried out under H_2, at temperatures ranging from RT to 150 ^{0}C. Reactions over several polymers (PS, PPO, VDF-CTFE copolymer) were carried out in a glass FP reactor using different catalyst loading (2.5 - 5 metal mol %) and H_2 pressures (3 – 7 bar).

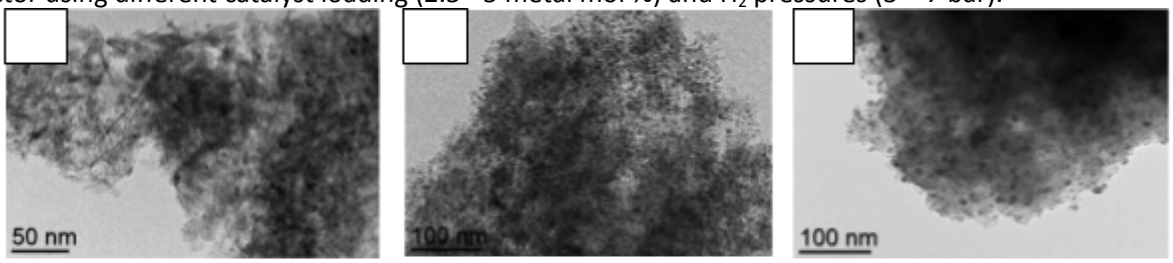
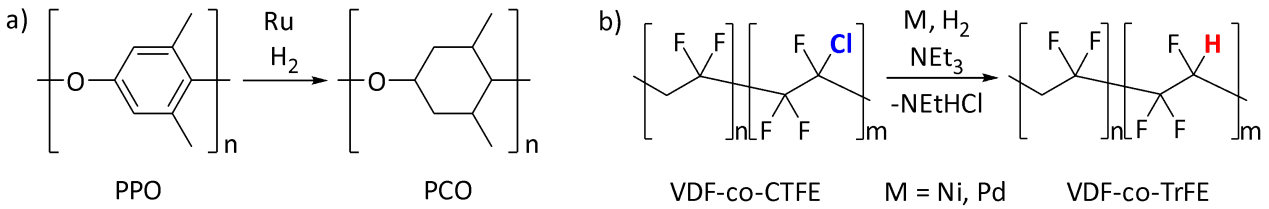


Figure 1. *TEM pictures of selected Ru (a), Pd (b) and Ni (c) supported catalyst.*

Results and discussion. Ru NPs (Figure 1a) have been found to be active in aromatic polymer hydrogenation (PS, PPO), with low hydrogenolysis level (scheme 1a). Remarkably, different semi aromatic polymers could be obtained by modifying reaction temperature and support selection. Moreover, Pd and Ni NPs (Figure 1b and 1c, respectively) achieved selective hydrodechlorination (up to 80%) of VDF-CTFE, without affecting the fluorine moieties (scheme 1b). All these reactions were carried out under mild conditions (3 - 7 bar of H2, 423 K as maximum temp.).



Scheme 1*. Hydrogenation of PPO (a) and Hydrodechlorination of VDF-co-CTFE (b).*

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Selective Glucose oxidation towards Gluconic acid using a highly defective Graphitic Carbon Nitride under mild conditions

Maria Ventura[1]*, Jaime Mazario[2], Marcelo E.Domine[3], Juan Antonio Melero[1]
[1]*Chemical and Environmental Technology Departament, ESCET, Universidad Rey Juan Carlos, Madrid, Spain*
[2]*Laboratory of Physics and Chemistry of Nano-Objects, LPCNO, Toulouse, France*
[3]*Instituto de Tecnología Química, Valencia, Spain*
[*]*maria.ventura@urjc.es*

Introduction. The necessity to diversify our resources and the general trend of reducing our CO_2 footprint has opened opportunities to produce chemicals, materials, and fuels from renewable feedstocks.[1] In this context, the sugar platform is now the subject of intense investigations. Gluconic acid is a highly valuable chemical used as a platform molecule in many industrial processes. Nowadays, its synthesis is achieved via the enzymatic oxidation of D-glucose, which has many disadvantages, such as poor productivity and wastewater generation. Precious metals have also been extensively tested for this process, but their practical applications are impeded by low selectivity, large energy consumption and high cost. Therefore, the development of more effective and cheaper processes should be a promising strategy for traditional technologies. In this context, photocatalysis has been developed and some authors reported the use of graphitic carbon nitride (g-C_3N_4) as semiconductor material, but giving low selectivity to the desired products.[2] In this work, a highly defective g-C_3N_4 was synthesized, to which different Fe quantities were incorporated by a solvothermal method. The solids were successfully used as photocatalysts in the oxidation of glucose in the presence of H_2O_2. In addition, cellulose degradation to glucose and subsequent oxidation to the main products, was also carried out in the presence of H_2O_2 or air. Reaction conditions: catalysts loading, substrate and oxidant concentration and time were optimized.

Experimental/methodology. Catalysts were synthesized by a solvothermal method in a controlled air atmosphere using different precursors ratio (urea and guanidine chloride (GnCl)) and various Fe wt%. The catalytic reactions were performed in a glass reactor under irradiation between 280 and 380 nm, using the optimized concentration of H_2O_2, [sustrate]=0.5 g/L, and 15 wt% of catalysts. The reaction medium withdrawal was characterized by HPLC-RI using a ROA-sugar as column. Catalysts were fully characterized by XRD, SEM, TEM, XPS, ICP, BET, Raman and elemental analysis before and after reaction.

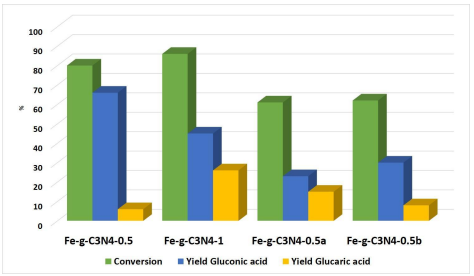

Figure 1. Catalytic oxidation of glucose. Reaction conditions: time=120 min, catalyst=15% w/w ,[Glucose]=0.5 g/L VH_2O=5 mL, irradiation=280-380 nm, [H_2O_2]=30% a. 4% of Fe; b. Cellulose was used as substrate

Results and discussion. Figure 1 shows the main results of the oxidation of glucose to gluconic or glucaric acid. The catalysts synthesized with a ratio 1Urea:0.5GnCl (Fe-g-C_3N_4-0.5) show the best selectivity to gluconic acid, 82%. Changing the precursor ratio (1:1;Fe-g-C_3N_4-1) shifts the reaction's selectivity, making gluconic acid selectivity decrease to 50% and glucaric acid increase to 30%. A more defective solid might enhance selectivity to gluconic acid, which also increases the BET surface area, suggesting that structural changes may have caused more effective oxidation. Additionally, the amount of Fe plays an important role in catalytic activity, with solids containing at least 2% Fe having the highest activity and selectivity. When high quantities of Fe are used, the dispersion of this Fe is less effective, which results in a lower conversion. Excitingly, gluconic acid was also produced by degrading cellulose to glucose and then oxidizing it to gluconic acid using the most active catalyst, achieving an excellent yield and outlining the potential of this catalytic system. Additionally, air as oxidant was tested, but conversion and yield decreased considerably. After 5 consecutive runs, the optimal catalyst shows high recyclability and a slight decline in conversion as well as an increase in selectivity toward the main products. There will be a discussion of the features of the catalysts, SEM and XPS mainly, and the hypothesis as to why such a good yield of gluconic acid can be achieved. This work opens the possibility of obtaining valuable gluconic acid from solid waste such as cellulose using a new catalytic process.

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MOF-Derived Co/N Doped Carbons for the Nitroarene Hydrogenation Reaction

D. Villalgordo Hernández[1], E.V. Ramos Fernández[1], J. Narciso[1]

[1]Instituto Universitario de Materiales (IUMA), Inorganic Chemistry Department, University of Alicante, Alicante, Spain
[*]dvh5@gcloud.ua.es

Keywords: MOFs, doped carbons, heterogeneous catalysis, nitroarene hydrogenation.

Introduction.

Reduction of nitroarenes is an efficient route for the production of functionalized anilines which are widely used in several chemical industries including pharmaceuticals, agrochemicals, dyes and polymers. Conventional processes applied in industry consist of non-catalysed reactions generating great amounts of waste products. There has since been an intensive research on heterogeneous catalysts towards the efficient and selective transformation of nitroarenes with various reducing sites into functionalized anilines. Supported metal catalysts such as platinum supported nanoparticles appear as a highly efficient option for this reaction. However, its lack of chemoselectivity and high cost raise the need for an alternative. Co-N-C are found to be extremely active and selective in nitroarene hydrogenation. Thus in this work a series of ZIF-67 (a Co and N containing MOF) derived carbons, with high content in Co and N have been obtained.

Experimental/methodology.

A simple room temperature synthesis has been carried out to obtain ZIF-67. Once the MOF is obtained it is pyrolized at various temperatures between 600-1000 °C in N_2 atmosphere. In some cases a Co leaching step has been performed.

Results and discussion.

A series of activated carbons have been obtained by pyrolisis of a Co and N containing MOF such as ZIF-67 in order to obtain a highly doped carbon material with a high density of active sites of the type Co-N which allow for the activation of the nitro group by means of the N sites as well as H_2 by the Co ones. A varying N content has been observed with its decrease as the carbon's porosity develops. Also a cobalt leaching process with 0'1 M HCl has beed tested to study carbons with a lesser content of Co which will be much more dispersed in the carbon structure. The greater dispersion of this theoretical active site appears to have a direct impact on its efficiency, as can be seen in Figure 1.b), reaching a complete conversion with a 100 % selectivity in half the time than its more concentrated counterpart.

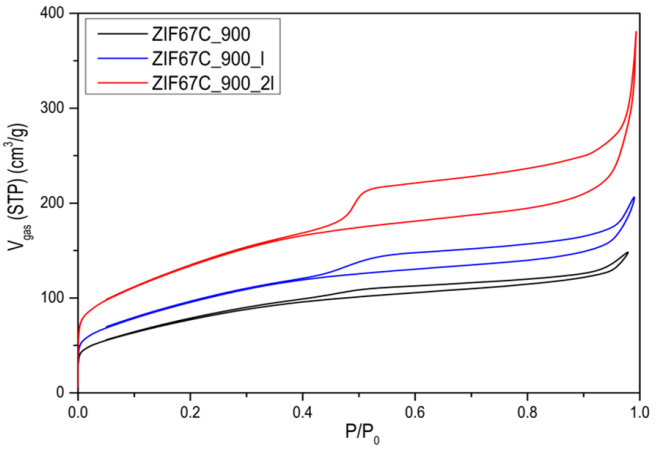
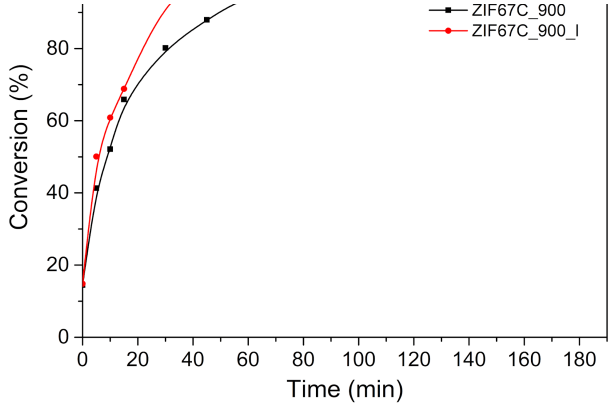


Figure 1. a) N_2 adsorption isotherm for a series of ZIF-67 derived carbons, b) conversion rate of 4-Chloronitrobenzene for two carbonized ZIFs with varying Co content.



Pickering interfacial catalysis on the particles-stabilized foams

M. Pera-Titus[1*], K. Wang[1], S. Zhang[2], D. Dedovets[2],

[1]*Cardiff university institution, Cardiff University, Cardiff, United Kingdom*
[2]*Laboratoire du Futur (LOF), UMR 5258 CNRS-Solvay-Université Bordeaux, Pessac Cedex, France.*
[*]*PeraTitusM@cardiff.ac.uk*

Keywords: Pickering foams, Interfacial catalysis, POSS, Janus particles

Introduction. Gas-liquid-solid (G-L-S) reactions are widespread in the chemical industry. State-of-the-art G-L-S reactors are affected by the low gas solubility in liquids and mass transfer limitations due to low G-L and L-S specific interface areas. In practice, high pressure is often required to boost the gas solubility and promote mass transfer. A way out of these shortcomings is to engineer G-L-S reactors based on particle-stabilized microbubbles for conducting catalytic reactions at near-ambient pressure. This requires surface-active heterogeneous catalysts able to adsorb and self-assemble at the G-L interface (**Figure 1a**).
Herein, we rationally designed three particle designs bearing flurionated chains and Pd nanoparticles to generate non-aqueous catalytic foams (**Figure 1b**): (1) organosilicas with randomly distributed fluorinated chains; (2) amphiphilic 'Janus' organosilicas including oleophobic (or gasphilic) and oleophilic hemispheres, and (3) polyhedral oligomeric silsesquioxanes (POSS) combined with particles in (1).

Experimental/methodology. Fluorinated organosilicas (364 nm) (1) were synthesised by the Stöber method using 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFDTES), (3-mercaptopropyl-triethoxysilane (MPTES) and tetraethylorthosilicate (TEOS) precursors, with MPTES/PFDTES and TEOS/PFDTES molar ratios of 1 and 4, respectively.[1] The Janus silica particles (250 nm) (2) were synthesized by sequential grafting of PFDTES and MPTES in each hemisphere using the emulsion template method. Finally, the POSS particles (1-3 nm) (3) were synthesized by hydrolytic condensation of triethoxylphenylsilane in basic conditions, and were further functionalized with trichloro(1H,1H,2H,2H-perfluorooctyl)silane.[2] Pd nanoparticles (1 wt%) were selectively deposited by wet impregnation (1) and sol-immobilization (2). The foaming and catalytic properties of the different particles were surveyed for the benzyl alcohol - xylene - air system. The particles were characterized by TGA, FTIR, and $^{13}C/^{29}Si$ MAS NMR.

Results and discussion. The different particles exhibited a divergent catalytic performance in the aerobic oxidation of benzyl alcohol in xylene (1:1 v/v) at near-ambient pressure, which was correlated to the foamability. Fluorinated organosilicas (1) exhibited high activity at a stirring rate >750 rpm by generating foams with intermediate stability. Janus particles (2), with much lower fluorine content (7.8% vs 33%), displayed comparable foamability and activity. However, these particles required xylene to generate foams. In contrast, particle system (3) exhibited high foamability for pure benzyl alcohol, increasing the green footprint of the system. Foams could be generated for a broad library of organic solvents with different surface tension by simply tuning the ratio of Pd-containing fluorinated organosilica and POSS particles, which expands the utility and flexibility of the strategy.
In conclusion, the design of surface-active particles plays a crucial role in stabilizing non-aqueous foams and affects accordingly the catalytic activity for benzyl alcohol oxidation at near-ambient pressure.

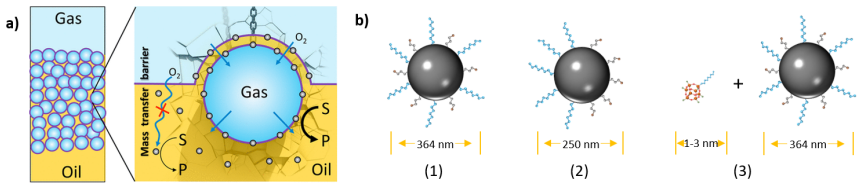


Figure 1. a) Schematic of G-L-S reaction on the Pickering foams. b) Sketch of three particles; (1) Fluorinated organosilica; (2) Janus particle; (3) POSS particles + Fluorinated organosilica.

Acknowledgments
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The Confinement Effect of CeO_2 Nanotubes Loaded Pd in CO_2 Hydrogenation to Methanol Reaction

Fengying Gao[1], Ning Wang[1*], Biaohua Chen[1]

[1]*Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, China*
[*]*Corresponding Author's E-mail address: ning.wang.1@bjut.edu.cn*

Keywords: CO_2 hydrogenation, methanol, CeO_2 nanotubes, confinement effect

Introduction. The confinement effect of nanotubes loaded metal in catalytic reaction has increasing attention. By now, the confinement effect of CeO_2 nanotubes (NTs) loaded Pd in CO_2 hydrogenation to methanol reaction has still few reports.

Experimental/methodology. The of CeO_2 nanotubes with three different tube diameters was synthetized by adjusting the concentration of urea and NaOH solution. The catalysts of Pd in CeO_2 NTs and Pd out CeO_2 NTs were synthesize by ultrasonic-assisted vacuum impregnation method and direct impregnation method, respectively.

Results and discussion. In this study, the average inner diameter of CeO_2 nanotubes was 13nm,11nm and 9nm, respectively. The size of Pd particles in CeO_2 NTs was smaller than out through CO pulse adsorption because of the effect of tubal confinement effect. The results of HAADF-Mapping and XPS could be indicated that the solid solution $Pd_xCe_{1-x}O_{2-\delta}$ formed on the CeO_2 nanotubes loaded Pd after calcining. This solid solution $Pd_xCe_{1-x}O_{2-\delta}$ was confirmed to promote CO_2 adsorption in CO_2 hydrogenation to methanol reaction[1]. The performance evaluation are shown in Fig. 1. We can find the CH_3OH selectivity showed an inverted U-type trend as the inner diameter of CeO_2 NTs decreases and the CH_3OH selectivity of Pd in CeO_2 NT were higher than that of Pd out CeO_2 NT, simultaneously, the CH_3OH selectivity of Pd in CeO_2 NT 12nm was the highest value (42%). However, the CO_2 conversion showed the opposite trend. And the CO_2 conversion of Pd in CeO_2 NT were lower than that of Pd out CeO_2 NT. We could tentatively speculate using these results that the smaller particle size promoted the improvement of methanol selectivity and the higher CO_2 conversion was because of the higher amount of Pd^{2+} in the solid solution $Pd_xCe_{1-x}O_{2-\delta}$ of Pd out CeO_2 NTs. This work provides new insights into the confinement effect of metal oxide nanotubes.

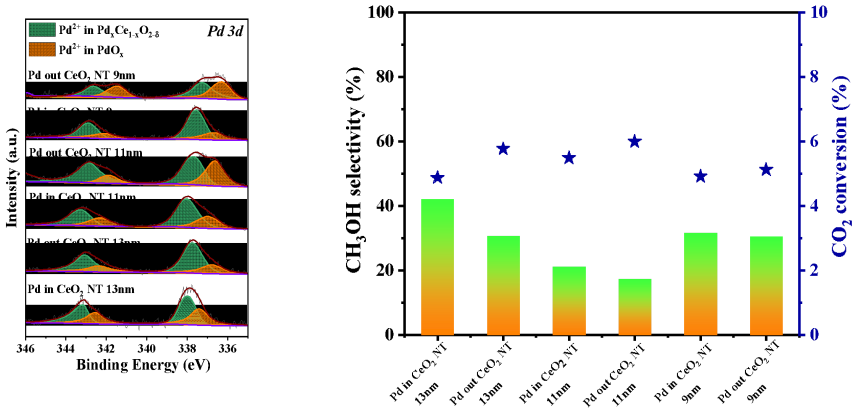

Fig. 1. XPS of Pd/CeO_2 NTs and the comparison of the catalytic performance of Pd/CeO_2 NTs in CO_2 hydrogenation to methanol reaction. Reaction conditions: 200mg catalyst,240°C, 3 MPa, CO_2:H_2:N_2=22:66:12, 10 mL min^{-1}, WHSV=3000 mL g_{cat}^{-1} h^{-1}

Acknowledgments

This research was supported by the National Natural Science Foundation of China (No.22176006, 22178011, 22278008).

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High temperature H_2 purification and water splitting performances of Pt deposited over dense ceramic membranes

P. Gramazio[1,2], A.Fasolini[1,2], A. Bartoletti[3], A. Gondolini[3], E. Mercadelli[3], A Sanson[3], and F. Basile[1,2]
[1]*Department of Industrial Chemistry "Toso Montanari", University of Bologna, Bologna, Italy*
[2]*Center for Chemical Catalysis - C[3], University of Bologna, Bologna, Italy*
[3]*CNR - Institute of Science and Technology for Ceramics (former ISTEC), Faenza, Italy*
[*]*f.basile@unibo.it*

Keywords: Hydrogen, Water splitting, Pt deposition, ceramic membranes, H_2 purification

Introduction.

Hydrogen economy development is becoming a priority among the EU countries and is needed to fulfill the clean energy transition. However, the immediate availability of large amounts of green H_2 is hold back by scale up issues and the production and utilization of blue hydrogen is needed to speed up the development of the H_2 infrastructure. Blue hydrogen refers to fossil based hydrogen integrated with carbon dioxide sequestration in processes such as hydrocarbon reforming or catalytic partial oxidation [1,2].

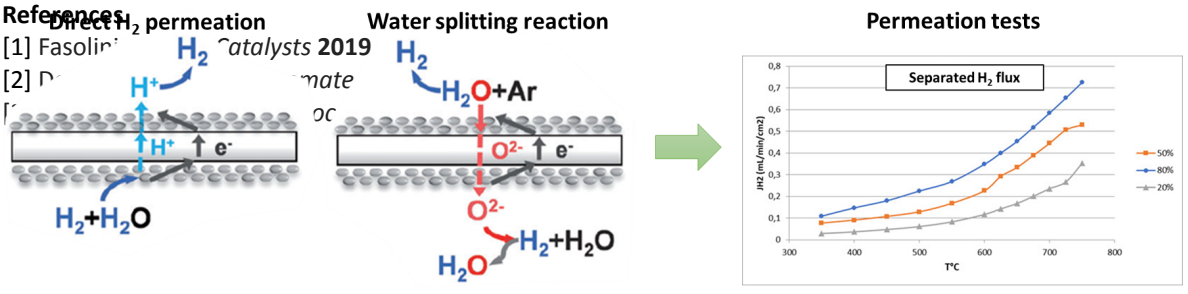
Here, gas separation is a crucial step to yield pure hydrogen. In this context, ceramic hydrogen permeation membranes are a breakthroiugh system able to operate at the high temperatures used in the hydrogen producton processes (>500°C) unlocking the possibility of processes intensification. These membranes is based on a composite forming a thin dense ceramic layer allowing the permeation of H^+, e^- and O^{2-}. The dense layer can be thinned by the production of a porous matrix (asimmetric membrane) that ensure the mechanical stability of the membrane system, allowing a higher permeation flux [3]. Here asimmetric dense ceramic membranes have been produced, to be applied, after the deposition of a Pt catayst, in the separation of hydrogen at high temperature.

Experimental/methodology

BCZY-GDC ($BaCe_{0.6}5Zr_{0.20}Y_{0.15}O_{3-\delta}$ - $Gd_{0.2}Ce_{0.8}O_{2-\delta}$) membranes with a porous-dense architecture were obtained by tape casting or freeze casting process with screen-printing. Pt was deposited over the membrane by impregnation, the membrane morphological properties were characterized and the hydrogen permeation tests were carried out in a double chamber reactor feeding a mixture of H_2O, He and H_2 at one side of the membrane and Ar and H_2O as sweep gas at the other side.

Results and discussion.

The performances of the produced membranes were investigated modifying the operative conditions with particular attention to H_2 concentration and the operative temperature. The hydrogen permeation through the dense layer was postively affected by temperature and partial pressue and was related to two main phenomena: (i) the permeation of hydrogen as proton and electrons and (i) the possibility of occurrence of water splitting to produce hydrogen with inverse permeation of O^{2-} and their reaction with H_2 at the hydrogen rich side of the membrane and thus producing as reactions sum the transfer of hydrogen from retentate to permeate (WS). The latter mechanism became predominant above 650°C allowing to push the hydrogen separation. From a catalytic point of view water splitting was highly affected by Pt distribution along the membrane. Here, its deposition was optimized and resulted in increased WS and H_2 permeation.



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Waste to Wealth: Fluid Catalytic Cracking Catalyst Synthesized from Solid-Waste Coal Gangue Minerals

Ruoyu Wang, Ye Song, Xue Yang, Wei Lin*

SINOPEC Research Institute of Petroleum Processing Co., Ltd., Beijing, China
**linwei.ripp@sinopec.com*

Keywords: coal gangue, Y zeolite, solid waste, self-combustion-depolymerization, FCC catalyst.

Introduction.

Globally, explorating efficient utilization technologies for coal gangue, a notorious hazardous solid waste, is one of the most important issues among current sustainable development topics. Herein, a green and energy-efficient self-combustion-depolymerization (SCD) approach is proposed to activate coal gangue into highly reactive silica and alumina species for in-situ crystallization of fluid catalytic cracking (FCC) catalysts[1-3].

Experimental/methodology.

FCC catalysts (SCD-Y) bearing in-situ generated Y zeolites can be readily fabricated via hydrothermal synthesis. In addition to conventional analytical characterization techniques, temperature-distance profiles acquired by a lab-scale drop-tube furnace (DTF) was used to evaluate the self-combustion behavior and the obtained SCD-Y were analyzed by X-ray micro-computed tomography (μ-CT).

Results and discussion.

Taking advantage of the heat released by the self-combustion of coal residue, the SCD activation of kaolin-type CG can be achieved at a medium temperature much lower than that required by natural kaolinite. Using microspheres mainly composed of SCD-CG as zeolization precursors, FCC catalysts bearing in-situ generated Y zeolites (SCD-Y) have been synthesized under hydrothermal conditions, and the zeolite crystals are fully exposed on its external surface. The as-prepared SCD-Y has a high crystallinity of ca. 50 % and a well-developed intraparticle macro-, meso- and microporosity, as revealed by BET, Hg intrusion and μ-CT. A comprehensive dissolving-crystallization microscopic model corresponding to the SCD-Y zeolitization process is proposed on the basis of kinetic study. Significantly, SCD-Y exhibits superior catalytic performance for cracking and prominent anti-deactivation properties for heavy oil conversion, demonstrating a gasoline boosting effect while suppressing dry gas and coke formation. Remarkably, the overall energy consumption (Etot) using this SCD approach (1429.65 kgce/t product) is 33.5% lower than that of the conventional semi-synthesis route (2151.37 kgce/t product). The green synthesis of FCC catalyst can be successfully achieved following this proposed SCD approach, which opens a broad field for energy-saving and high-efficient ultilization of solid-waste coal gangue minerals.

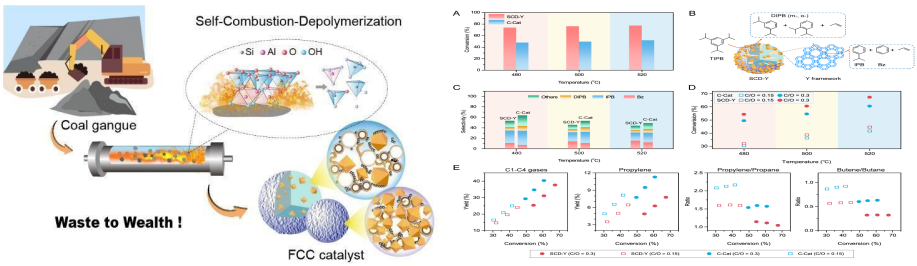

Fig.1 Schematic illustrations of the SCD approach proposed in this work using solid-waste coal gangue as the starting material. Fig.2 Catalytic cracking performances of SCD-Y and C-Cat

Acknowledgments

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Solvent-free crystallization of ZSM-5 zeolite on SiC foam as a monolith catalyst for biofuel upgrading

Yeqing Wang[1*], Qiuyan Zhu[2], Liang Wang[2], Zhixin Yu[3],Feng-shou Xiao[2*],

[1] *Institution of New Energy, College of Chemistry and Chemical Engineering, Shaoxing University, Shaoxing 312000, Zhejiang, China.*

[2]*Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310028, Zhejiang, China*

[3]*Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310028, Zhejiang, China*

[*]*wangyeqing@usx.edu.cn; fsxiao@zju.edu.cn*

Keywords: Zeolite, Pd@ZSM-5/SiC, Monolith catalyst, Solvent-free synthesis

Introduction

Zeolite-based catalysts are localized in fixed-bed reactors in the form of powdered microgranules or extrudates, which are extensively used in the current practical processes, but the mass transfer on these catalysts still needs to be improved. In most reactions, temperature differences in the reactor caused by limited heat transfer is also known to lead to unsatisfactory catalytic performance. In order to overcome these problems, we investigate a promising strategy in which zeolite crystals are coated onto a monolith support. In pioneering studies, coating zeolite-based catalysts onto an SiC matrix were generally synthesized using the conventional hydrothermal route. This strategy is not very effective due to the production of undesirable wastes.

Results and discussion.

Here, we report a solvent-free crystallization process to coat ZSM-5 zeolite crystals on a monolithic SiC foam with a honeycomb structure (ZSM-5/SiC), as shown in Fig.1. Characterizations of the ZSM-5/SiC by scanning electron microscopy, N_2 sorption, and X-ray diffraction indicate that the zeolite sheath has been ideally coated on the surface of the SiC foam with high purity and crystallinity. Fixing Pd nanoparticles within the ZSM-5 zeolite crystals delivers a bifunctional Pd@ZSM-5/SiC catalyst, which exhibits high activity and selectivity toward diesel range paraffins in the hydrodeoxygenation of methyl oleate, a model molecule for biofuel. In comparison to the powder Pd@ZSM-5, the Pd@ZSM-5/SiC monolith catalyst shows more efficiency, which is attributed to the fast mass transfer and high heat conductivity on the honeycomb SiC structure. The durability test indicates that the Pd@ZSM-5/SiC catalyst is stable under the reaction and high-temperature regeneration conditions.

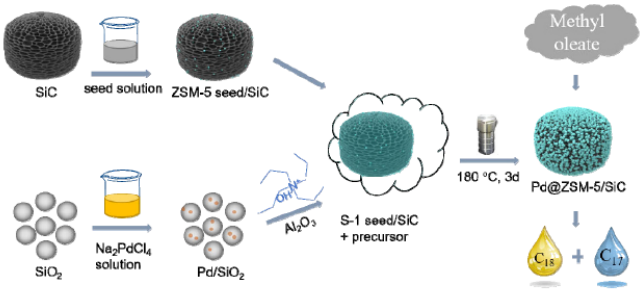

Fig. 1 Synthesis of ZSM-5/SiC.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (2018YFD1000806-01), National Natural Science Foundation of China (21822203, 91645105, 91634201), Natural Science Foundation of Zhejiang Province (LR18B030002), and the funding of central universities.

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Bimetallic platinum rhenium catalysts for efficient low temperature dehydrogenation of perhydro benzyltoluene

D. Strauch[1], B. B. Sarma[2], D. Doronkin[2], A. Zimina[2], E. J. Olivier[3], J.-D. Grunwaldt[2], P. Wasserscheid[1], M. Wolf[2*]

[1]*Forschungszentrum Jülich, Erlangen, Germany*
[2]*Karlsruhe Institute of Technology, Karlsruhe, Germany*
[3]*Nelson Mandela University, Gqeberha, South Africa*
[*]*moritz.wolf@kit.edu*

Keywords: Chemical hydrogen storage, LOHC, dehydrogenation, bimetallic, platinum, rhenium

Introduction. Hydrogen is considered a game changer in the global energy transition. However, while the gravimetric storage density of H_2 with a lower heating value (LHV) of 33.3 kWh kg^{-1} is excellent, the volumetric storage density at ambient pressure is as low as 0.003 kWh L^{-1}. In consequence, existing technical storage solutions either compress H_2 to high pressures of up to 850 bar or store it in its liquid state at -253 °C.[1] Liquid organic hydrogen carriers (LOHCs) represent an emerging alternative and highly attractive way to chemically store and release H_2, which avoids transportation and storage of molecular H_2. For example, benzyltoluene (H0-BT) can reversibly bind 6 mol of H_2 yielding perhydro benzyltoluene (H12-BT). Such storage and transportation of H_2 in form of diesel-like liquids allows for utilization of existing infrastructure for liquid fuels. H12-BT is non-flammable, has a wide liquid range and a storage density for H_2 of 6.2 wt%.[1,2] However, up to 30% of the LHV of the released H_2 must be expended to provide sufficient heat for the dehydrogenation step if no external heat streams are available. First demonstrations plants for H_2 release operate at temperatures exceeding 300 °C.[2] Lowering the temperature of H_2 release during dehydrogenation is of utmost importance to increase the overall efficiency. Here, the generally slower reaction rates and other challenges, such as product desorption, demand novel catalyst materials, which may strongly differ from existing commercial solutions.[2,3]

Experimental/methodology. Herein, bimetallic Pt-Re/Al_2O_3 catalysts with various Pt:Re ratios were prepared and characterized to study the low temperature liquid phase dehydrogenation of H12-BT. The catalysts were analyzed by means of temperature programmed reduction (TPR), high-resolution scanning transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (HRSTEM-EDX), and *in situ* X-ray absorption spectroscopy (XAS) during catalyst activation in H_2.

Results and discussion. The bimetallic Pt-Re catalysts exhibited a superior performance during dehydrogenation of H12-BT at low temperatures (Fig. 1). Here, optimization of the Pt:Re ratio is crucial, while calcination and reduction temperature have little influence. Sophisticated *in situ* characterization of the catalyst suggests mostly structural promotion of Pt by Re resulting in a robust catalyst with a significantly enhanced activity when compared to a monometallic Pt/Al_2O_3 catalyst. The preparation of the bimetallic catalyst was scaled-up and shaped supports were employed to bridge lab-based catalyst development and commercial application of this novel dehydrogenation catalyst. Lastly, selective sulphur poisoning[3] was successfully demonstrated to suppress side reactions combining an accelerated H_2 release in with high yields of H0-BT.

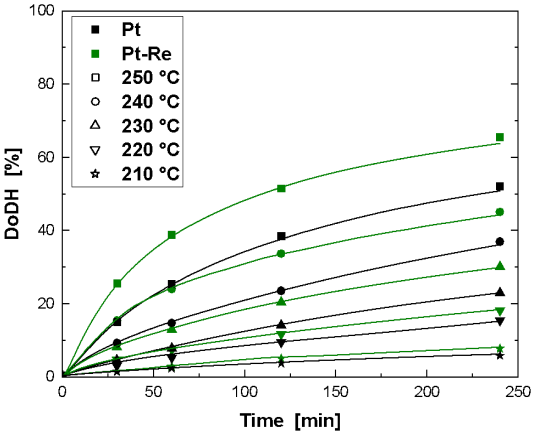

Fig. 1: Degree of dehydrogenation (DoDH) during semi-batch dehydrogenation of H12-BT at 1 bar using an optimized Pt-Re/Al_2O_3 catalyst in comparison to a Pt/Al_2O_3 catalyst.

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Kinetic analysis to describe Co-operative redox enhancement effects exhibited by bimetallic Au– Pd systems in aerobic oxidation

Oliver T. Wright[1*], Isaac T. Daniel[1], Liang Zhao[1], Donald Bethell[1], Mark Douthwaite[1], Samuel Pattisson[1], Richard J. Lewis[1], Ouardia Akdim[1], David J. Morgan[1], Steven McIntosh[2] and Graham J. Hutchings[1]

[1]*Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Cardiff University*

[2]*Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA, US*

[*]*WrightOT@cardiff.ac.uk*

Introduction.

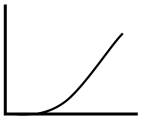
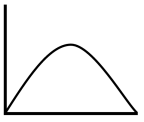
A potential key monomer in the industrial production of PET,[1] FDCA, can be produced *via* the full oxidative dehydrogenation of HMF utilising supported Au and Pd bimetallic catalysts. Recently, the separation of Au and Pd in supported bimetallic catalysts was demonstrated to enhance catalytic performance in such reactions through the coupling of separate redox reactions; an effect known as cooperative redox enhancement (CORE).[2] This effect differs from conventional synergistic interactions exhibited by Au-Pd bimetallic catalysts as the individual metallic properties, crucially, are unaltered. Deriving kinetic models based on our understanding of CORE, we can provide further evidence and acquire deeper understanding for CORE effects exhibited by bimetallic Au-Pd catalysts.

Experimental/methodology.

All the catalysts used in this study were prepared by the sol-immobilisation (SI) method, using polyvinyl alcohol as a stabiliser and carbon as the support. Catalysts were tested in glass reactors for the aqueous phase oxidation of HMF under O_2 (3 bar). Particle size distribution of the catalysts were determined using transmission electron microscopy (TEM) and metal oxidation states were probed by X-ray photoelectron spectroscopy (XPS). Au and Pd loadings were determined through catalyst digestion and Inductively Coupled Plasma Mass Spectrometry (ICP-AES).

Results and discussion.

TEM of the Au/C and Pd/C catalysts confirmed that the SI method was effective, with both catalysts exhibiting narrow particle size distributions of 3.0 and 4.3 nm, respectively. XPS analysis of the Au*4f* region and Pd*3d* region was conducted over the respective catalysts, confirming the metallic nature of the Au present. For the fresh Pd/C catalyst, a small proportion of Pd^{2+} was observed with a Pd^0 /Pd^{2+} at % ratio of 6.33. However, it is not anticipated that the proportion of Pd^{2+} present in the fresh Pd/C catalyst will influence the rate of reaction, due to the consideration that the electron transfer between both metals are non-limiting. Microwave digestion of the solid catalysts followed by ICP-AES analysis confirmed both Au/C and Pd/C had an accurate loading of 1.0 wt%. The catalysts were subsequently assessed for the aqueous phase oxidation of HMF, enabling the derivation of kinetic models. The Au monometallic system conforms to the kinetic model at low Au masses, showing evidence for coupling between DH and ORR half-cells, where an above-linear enhancement arises. At high masses of catalyst and throughout the Pd data set, a linear the relationship between activity and metal moles is overserved. When the combination of both catalysts in a physical mixture occurs, the activity exceeds the sum of the two monometallic systems and therefore illustrating the significant enhancement which is driven by the CORE effect.

Rate Equation	Graphical Prediction
$\frac{v_1}{[M]} = \frac{k_1^A f \cdot k_2^A f}{k_{-1}}$	$\frac{v_1}{[M]} \propto f^2$ Maxima: Au mol.% = 100 
$\frac{v_1}{[M]} = \frac{k_1^A f \cdot k_2^P f(1-f)}{k_{-1}}$	$\frac{v_1}{[M]} \propto f \cdot (1-f)$ Maxima: Au mol.% = 50 

Au/C and the Au/C and Pd/C systems.

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Gold(III)-Crosslinked Single-Chain Nanoparticles as Sonogashira Reaction Recyclable Homogeneous Catalytic

Haonan Xiang,[1] Wenbin Yi[1*]

[1]Nanjing *University of Science and Technology, Nanjing, P.R. China*
[*]*Corresponding Author's E-mail: yiwb@njust.edu.cn*

Keywords: Homogeneous Catalysts, Single-Chain Nanoparticles, Recyclable Catalysts.

Introduction. Chemical catalytic systems for industrial and laboratory use are of fundamental importance in our daily lives. Catalysts not only activate inert starting materials but also improve reaction conditions and product selectivity. However, there is a constant need for further development and improvement of homogeneous catalytic systems due to its higher catalytic activity but difficult to separate and tend to remain in the final product.[1] Indeed, such an extraordinary system already exists in nature: enzymes.[2] Driven by a carefully selected sequence of building blocks, the sulfur-containing macromolecular chains are a group of attractive modern materials, due to their fascinating properties such as metal coordination ability.[3] Therefore, the development of sulfur-containing single-chain nanoparticles to ligand precious metals to achieve recyclable homogeneous catalysis effect is highly imperative.

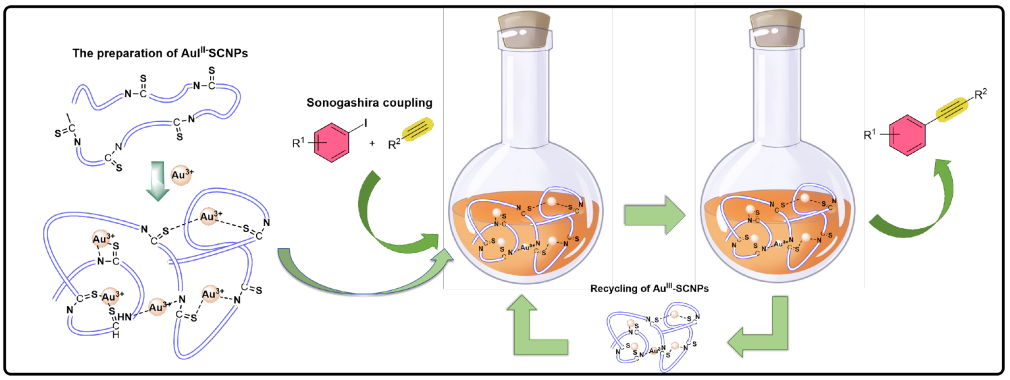

Figure 1. the preparation of gold(III)-SCNPs and its application in the Sonogashira coupling reaction

Experimental/methodology. Prepration of gold(III)-SCNPs: In a 10 mL aqueous solution of $AuCl_3$, ([Mn^+] = 100 mg/L, with 5 wt% HNO_3), 10 mg polythioamide was added respectively. After stirring at room temperature for 2 h, the suspensions were centrifuged for 10 min with a spin rate of 10000 r/min, and the solid gold(III)-SCNPs was filtered by a filter membrane with an aperture of 0.22 m.
Sonogashira coupling reaction: Iodobenzene, alkyne and K_3PO_4 were added in a Schlenk tube under N_2. Gold(III)-SCNP dissolved in dry DMF were subsequently added. The reaction mixture was stirred for 12 h at 120 ℃. The product yield was calculated by GC.

Results and discussion. In this work, benefit by the good solubility of the polythioamides prepared by secondary amines, the gold^{III}-SCNP can be the homogeneous gold catalyst in polar solvents and to bridge the gold catalyst gap between homogeneous activity and heterogeneous recyclability. To develop the practicality of this type of catalyst, Sonogashira coupling reaction can be realized with nearly 80% yield. To our delight, amplified gram-scale reaction and a wide range of Iodobenzenes and alkynes both participate in this gold catalys cross-coupling. Finally, we demonstrate that our current system allows for post-catalytic isolation and reuse of the gold^{II}-SCNP by precipitation in methanol and the activity of the recovered gold complexes was investigated in a second cycle of Sonogashira cross-coupling. With 1,2-diphenylethyne conversion of approximately 77%, the catalyst retains high catalytic activity, thus confirming them to be a recyclable homogeneous catalyst, obtaining high conversions while applying only 10 mol % of catalyst.

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Controlling the chemoselectivity of 3-nitrostyrene hydrogenation by modification of the interface of Pt catalysts

Lifeng Xiao[1*], Rongsheng Cai[2], Sarah Haigh[2], Meenakshisundaram Sankar[1*]

[1] *Cardiff Catalysis Institute, Cardiff University, Cardiff, UK*
[2] *University of Manchester, Manchester, UK*
** Meenakshisundaram Sankar: sankar@cardiff.ac.uk ; Lifeng Xiao:XiaoL6@cardiff.ac.uk*

Keywords: selective hydrogenation, strong metal-support interaction, interfacial site

Introduction. The hydrogenation of 3-nitrostyrene (3-NS) is a model reaction to probe the industrially relevant chemoselective reduction of a vinyl (C=C □ C-C) or nitro group (NO_2 □ NH_2) over a catalyst. Hutchings[1] and Corma[2] have proposed that strong metal-support may influence chemoselectivity towards 3-vinylaniline (3-VA) during this reaction. This work investigates how the interaction between metal (Pt) and support affects the chemoselectivity of this reaction between different supports (TiO_2 and Nb_2O_5). To further identify the active site for chemoselectivity, the interaction between metal and support was modified by preparing a catalyst using the sol-immobilization (sol-im) method and utilising further heat treatments to invoke changes in the interaction between metal and support. We found that interfacial sites played an important role in controlling chemoselectivity in this reaction.

Experimental/methodology. A series of 0.2wt%Pt/TiO_2 and 0.2wt%Pt/Nb_2O_5 catalysts were prepared wet-impregnation and sol-im method using PVA as stabiliser. A further heat treatment was applied Pt/TiO_2 sample to obtain the sample without PVA on the catalyst surface. The catalytic activity test was performed at 40 ℃ and 3 bar H_2. A comprehensive high-resolution microscopy (HAADF-STEM) study was applied to investigate these sample in morphology. CO-DRIFTS, XPS, XAFS and DFT experiments were also performed.

Results and discussion. Figure 1 shows that the chemoselectvity of Pt/TiO_2 is towards to 3-VA and keeping at high selectivity even at high conversion, whilst for Pt/Nb_2O_5, 3-NS hydrogenation is chemoselective to 1-ethyl-3-nitrobenznene (3-ENB). CO-DRIFTS and HAADF-STEM of these two catalsyts shows that the Pt particle structure is same. According to our further characterization by XPS, XAFS and DFT, the diference in the interfacial site between these two catalsyts determines whether the adsorption of nitro or vinyl group is more favourable, leading to an inversion in the chemoselectivity. To further demonstrate the site responsible for chemoselectivity, Pt/TiO_2 catalysts were prepared by sol-im and tested as-prepared and after a calcination step. STEM analysis revealed PVA was blocking the interaction of Pt with the support for the as-prepared catalyst. However, in the catalyst that underwent a further heat treatment, the Pt particle was observed to be in direct contact with the support with no residual PVA stabiliser around Pt particle using STEM imaging. As shown in Figure 2A, the catalyst prepared by Sol-im method and has no contact with the support, the selectivity is towards to 3-ENB. Whereas, the catalysts prepared without PVA or are subjected to further heat treatment to remove resiudal PVA, the selectivity is reversed to 3-VA. Our conclusion, combining the results of catalytic performance, is that the PVA blocked the interface of metal and support, which lead to the difference in chemoselectivity between these two samples and demonstrates the importance of the Pt/TiO_2 interface for the selective reduction of the 3-NS to 3-VA.

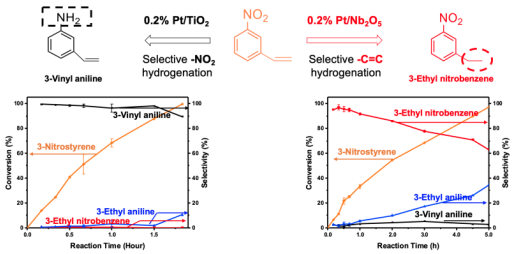

Figure 1. Catalytic performance of sample prepared by wet-impregnation with different supports.

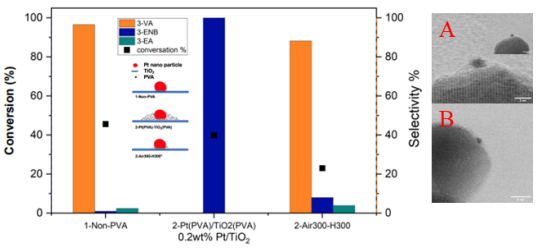

Figure 2. Catalytic performance of sample prepared by sol-im sample and sol-im with further heat treatment and wet-impregnation.

Acknowledgments

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Fabrication of Nanocatalysts using Flame Aerosol Synthesis Method

Yuan Sheng[1], Guanyu Liu[1], Mudi Wu[1], Markus Kraft[2,3], Rong Xu[1,2*]

[1]*Nanyang Technological University, Singapore*
[2]*Cambridge Centre for Advanced Research and Education in Singapore (CARES), Singapore*
[3]*University of Cambridge, United Kingdom*
[*]*rxu@ntu.edu.sg*

Introduction. Flame aerosol synthesis (FAS) is an established method of synthesizing nanoparticles. It remains to account for the production of the majority of commercial nanoparticulate products including but not limited to carbon black, fumed silica, and the benchmark photocatalyst, P25 TiO_2.[1,2] FAS is a continuous flow process where precursor vapors or micro-droplets are fed to a flame, pyrolyzed, and form nanoparticles as an aerosol.[3] The recovery of the particles from the aerosol is less energy consuming than separation of a slurry due to the difference in viscosity, and the waste treatment is simpler because with properly selected precursors, the exhaust of FAS is hardly different from that of a gas burner. In laboratory studies, the high reaction temperature of FAS (typically >1500 °C) and the tunable redox environment provide a versatile platform that has facilitated the synthesis of almost all nonradioactive metal oxides and noble metal nanoparticles.[3] They have found a wide range of applications in thermo- and photocatalysis.[4-7] Moreover, by aiming a particle-laden flame at a substrate, nanostructured films can be prepared without separating the particles, which is an attractive synthesis strategy for electrochemical devices.[8]

Experimental/methodology. In our lab, we have fabricated various catalysts using the FAS method,[5,6,9,10] including NiFe-P for electrochemical oxygen evolution, Cu for CO_2 electrochemical reduction and NiO_x-$SiAlO_x$ for oligomerization of ethylene.

Results and discussion. We have shown that FAS is a promising alternative method for fabrication of nanocatalysts with controllable properties.

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Cyano-Bridged Metal Complexes Containing Lanthanoid Ions as Heterogeneous Catalysts for Organophosphate Hydrolysis

Yusuke Yamada[1,2*], Yusuke Seki[1], Takashi Nakazono[2], Hiroyasu Tabe[3]

[1]*Department of Chemistry and Bioengineering, Osaka Metropolitan University, Osaka, Japan*
[2]*Research Institute for Artificial Photosynthesis (ReCAP), Osaka Metropolitan University, Osaka, Japan*
[3] *Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Kyoto, Japan*

[*]*ymd@omu.ac.jp*

Keywords: pesticide, insecticide, europium, terbium

Introduction. Residual organophosphates after using pesticides and insecticides found in soils, irrigation, and air should be removed to prevent adverse effects on human health. The residual organophosphates are usually removed by suitable adsorbents such as activated carbon, however, those at high concentrations cannot be removed entirely due to the limited capacity of the adsorbents. Some metal ions including lanthanoid ions (Ln^{III}; Eu, Tb, etc) have been reported to act as homogeneous catalysts highly active for the hydrolytic reaction in an aqueous solution. Heterogenization of the metal ions is strongly demanded for easy handling, high robustness, and facile separation after the catalytic reactions. However, the heterogenization often results in reducing the catalytic activity due to the limited diffusion of substrates and specific adsorption of products on the catalyst surfaces. We report herein how to heterogenize Ln^{III} ions in various matrices without losing catalytic activity for *p*-nitrophenyl phosphate (*p*-NPP) hydrolysis. The heterogenization of Ln^{III}-ion catalysts was examined by three methods, i.e., preparation of lanthanoid oxides ($Ln^{III}_2O_3$), immobilization of the Ln^{III} ions on silica-alumina (Al-SiO_2) by the cation-exchange (Ln^{III}/Al-SiO_2), and cyano-bridged heterometallic coordination polymers containing Ln^{III} ions ($[Ln^{III}(H_2O)_x]_y[M^C(CN)_6]$, Ln = Tb or Eu; M^C = Fe^{III} or Ru^{II}; $x \geq 2$) [1]. A class of cyano-bridged coordination polymers have been reported to exhibit high catalytic activity for the reaction.

Experimental. $[Ln^{III}(H_2O)_x]_y[M^C(CN)_6]$ complexes were synthesized as precipitates by mixing $K_a[M^C(CN)_6]$ and Ln^{III} ions in aqueous media. *p*-NPP hydrolysis was performed in a mixed solution of HEPES buffer (pH 7.0) and ethanol (3:7 (v/v)) containing *p*-NPP and $Ln^{III}_2O_3$, Ln^{III}/Al-SiO_2 or $[Ln^{III}(H_2O)_x]_y[M^C(CN)_6]$ at 60 °C.

Results and discussion. The conversions of *p*-NPP to *p*-nitrophenol (*p*-NP) after 72 h for the reaction systems containing $Eu^{III}_2O_3$ (52%) and Eu^{III}/Al-SiO_2 (51%) were lower than that of corresponding Eu^{III} ions acting as homogeneous catalysts in the reaction solutions (64%). On the other hand, the conversions of *p*-NPP for the reactions systems employing $Eu^{III}[Co^{III}(CN)_6]$ and $[Eu^{III}(H_2O)_x]_y[Ru^{II}(CN)_6]$ (88% for each at 72 h) were obviously higher than that of Eu^{III} ions (64%) because of the enhanced surface acidity of the coordination polymers with trivalent Co^{III} ions compared with that of divalent Ru^{II} ions. Similar results were obtained for the reaction systems containing Tb^{III} ions instead of Eu^{III} ions. Thus, incorporation of Ln ions in cyano-bridged metal complexes is an effective method for heterogenization of catalytically active metal ions without losing but enhanced catalytic activity.

Acknowledgments

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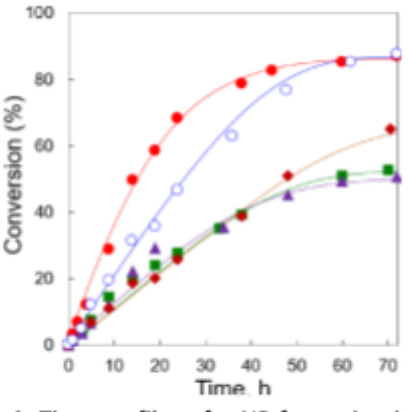

A metal-free carbon catalyst for oxidative dehydrogenation of aryl cyclohexenes to produce biaryl compounds

Mingze Yang, Yongdan Li*

Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Espoo, Finland

** Corresponding author. Email: yongdan.li@aalto.fi*

Keywords: Biaryl synthesis, Carbocataylsis, Oxidative dehydrogenation

Introduction. Biaryls are a common structural unit in a wide range of fine chemicals, which find application in various fields, e.g., agrochemicals, pharmaceuticals, precursors of electronic materials, and ligands to metal ions or atoms [1]. This unit is also vastly present in natural products [1]. According to an early 2000s article, the biaryl structure exists in 4.3% of the known drugs, making it a crucial subunit for the pharmaceutical industry [2]. To avoid the toxic substrates and an unstable and precious catalyst in classic Pd-catalyzed coupling [3], the direct aromatization of functionalized aryl cyclohexenes via oxidative dehydrogenation (ODH) is a practical and potentially environmentally benign way [4]. Traditional ODH reactions are catalyzed by various transition metal and metal oxide catalysts. Over the past decade, carbon has been developed as a metal-free and green alternative catalyst for ODH reactions [5]. A wide range of carbon materials have been utilized as catalysts for ODH reactions, including both well-defined nanostructures and amorphous carbon. In addition, a broad range of substrates have been investigated However, to the best of our knowledge, the carbon-catalyzed ODH reaction of aryl cyclohexenes in the liquid phase to access biaryls is currently unreported. In this work, the carbon-catalyzed ODH of aryl cyclohexenes to biaryls is investigated and the applicability of this reaction is studied with 15 different substrates. The mechanism and active site of carbon catalysts are also discussed.

Experimental/methodology. Catalyst preparation: The commercial active carbon was treated with acid to remove all the impurities and treated with Air and Ar under heating respectively. The obtained sample was donated as air-oxidized active carbon(oAC_{air}). Catalytic test: The reactions were carried at 140 ^{o}C for 28 h under 5 bar O_2 pressure. The reactions were monitored with GC-FID and GC-MS (dodecane as the internal standard). Characterization: XPS, BET, FT-IR, SEM and Raman spectra were applied to characterize the catalysts. Catalyst model compound experiments, functional group blocking experiments and the effects of additives were carried out to confirm the mechanism.

Results and discussion. The developed oAC_{air} catalyst offers improved efficiency, compared to other reported carbon allotropes like CNTs and graphite and is also comparable with metal catalysts. With the aid of kinetic study, the oAC_{air} catalyst exhibited the highest activity (rate constant k= 9.1×10^{-2} h^{-1}) and the activation energy was 54.5 kJ·mol^{-1}. The catalytic behaviour and robustness of the oAC_{air} were confirmed by recyclability tests, which showed remarkable stability over six cycles. XPS analysis and BET analysis indicated the direct relationship between oxygenated surface area and activity. The dramatic decrease in the activity of the carbonyl group blocked catalyst and similar catalytic performance of phenanthrenequinone confirmed that the quinoidic carbonyl group is the active site of oAC_{air} in the ODH reaction. The quinoidic redox cycle mechanism is proved via the active site and the acid effect, which is consistent with the carbon-catalyzed ODH of other substrates. Hammett plot suggests a positively charged intermediate and the structure of this intermediate is proposed. The substrate scope consisting of 15 differently substituted aryl cyclohexenes has proven the wide applicability of this ODH reaction.

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An Unusual Red Carbon Nitride to Boost the Photoelectrochemical Performance of Wide Bandgap Photoanodes

Y. Yang[1,2], Y. Li[2], S. Li[1] and J. Wang[2]

[1] *School of Materials and Chemical Engineering, Henan University of Urban Construction, Henan 467000, P. R. China*

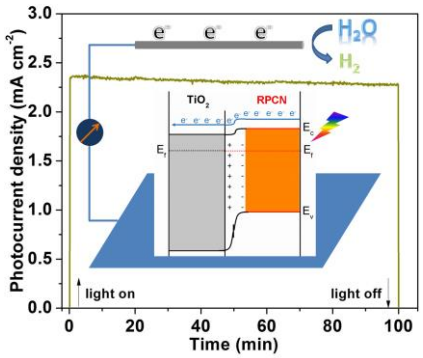
[2] *School of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, P. R. China*

[*] *Corresponding Author's E-mail address : ylyang@huuc.edu.cn*

Keywords: ed-shift absorption, alkali-atom modification, red-colored carbon nitride, TiO2 photoanode, photoelectrochemical water splitting

Abstract: Tuning the bandgap of a semiconductor to achieve strong band-to-band visible light absorption is highly desirable but challenging for photocatalysis. This work presents a facile molten-salt-assisted route to prepare red-colored polymerized carbon nitride (RPCN) nanosheets with a remarkable redshifted absorption and narrowed bandgap of 1.9 eV. Both experimental findings and theoretical calculations reveal that alkali heteroatoms are effective to tune the surface and electronic structures of carbon nitride, resulting in significantly reduced bandgap and excellent solubility. The RPCN-sensitized TiO_2 nanorod-based photoanode generates an impressive photocurrent density of ≈2.33 mA cm^{-1} at 1.23 V versus reversible hydrogen electrode under Air Mass 1.5 G illumination without any cocatalyst, which is 2.6 folds higher than that of the bare TiO_2 photoanode. The new findings in this work could inspire the electronic structure engineering of semiconductor photocatalysts to greatly enhance the visible light absorption and provide a generic strategy to enhance the photoelectrochemical performance of wide-bandgap semiconductor photoelectrodes.

Results and discussion.



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Controlled Molecular-Weight Polymerization of Norbornenes Containing *Bay*-Functional Perylene Diimides

Hassan S. Bazzi[1,2*], Santhosh Kumar Podiyanachari,[1] Mohammed Al-Hashimi[1]

[1]*Division of Arts & Sciences, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar*

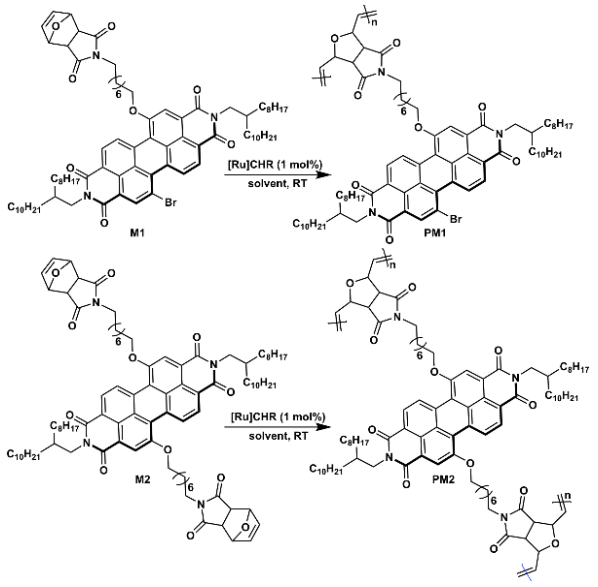
[2]*Department of Materials Science & Engineering, Texas A&M University, 209 Reed MacDonald Building, College Station, TX 77843-3003, United States*

**bazzi@tamu.edu*

Introduction. Perylene diimide (PDI) has attracted great interest as an electron-deficient core featuring excellent optical, chemical, and thermal stabilities.[1] Polymeric systems containing PDIs have excellent flexibility, photo- and chemical-stabilities.

Experimental. Ring-opening metathesis polymerization[2] (ROMP)-derived mono-alkoxy poly(oxanorbornene imide) **PM1** and 1,7-di-alkoxy **PM2** bearing *bay*-functionalized perylene diimides (PDIs) were synthesized using ruthenium-alkylidene metathesis initiators (Scheme 1).

Results and Discussion. The monoalkoxy-derived PDI-based non-ladderphane polymer **PM1** displayed 67 to 77% of the *trans* olefin content in the polymer chain depending on the initiator used for the polymerization. In the case of the symmetrical 1,7-dialkoxy-derived PDI-based polymer **PM2** having the ladderphane type-structure, showed a significant amount of *cis* and *trans* olefin contents in the polymer chains, irrespective of the type of initiators used for the polymerization. ROMP of both monomers **M1** and **M2** proceeded in a well-controlled manner with a linear dependence of molecular weight on the monomer/initiator ratio. Optical properties of the ladderphane-based **PM2** and non-ladderphane-based **PM1** were characterized in both solution and the film state. X-ray diffraction (XRD) analysis for all the polymers showed significant π-stacking in the thin film state and the film morphology examined by AFM elucidated homogenous smooth polymer surface for both polymers in general, but with some irregularities observed for **PM1**.[3]



Scheme 1. Ring-opening metathesis polymerization of oxanorbornene-based *bay*-functional perylene diimides

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Kinetic and computational studies of CO oxidation and PROX on Cu/CeO_2 Nanospheres

N. Yigit[1], P. Tangpakonsab[1], A. Genest[1], A.Meral[1], G. Rupprechter[1*]

[1] *Institute of Materials Chemistry, TU Wien, Vienna, 1060, Austria*
[*] *guenther.rupprechter@tuwien.ac.at*

Keywords: CuO, CeO_2, TPR, XRD, PROX, DFT

Introduction.

Hydrogen production and purification are industrially important processes. Hydrogen is used for the synthesis of ammonia [1] and of numerous other chemicals [2]. H_2 is also used in fuel cells, but even ppm concentrations of CO poison the Pt electrodes [3]. The catalytic preferential CO oxidation (PROX) is thus a key reaction for removing traces of CO from the desired H_2-rich stream dedicated for fuel cells. Transition metal oxides, especially Cu-based catalysts has been shown to be efficient at low temperature for the PROX reaction.

Experimental/methodology.

The synthesis of CuO/CeO_2 nanosphere catalysts is based on the hard template method [4], with CuO nanoparticles loaded on the outer surface of hollow CeO_2 nanospheres by a layer-by-layer deposition technique. The presented characterization includes X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), CO- and H_2- temperature programmed reduction (TPR). For catalytic performance of PROX, the focus was on the effect of various pretreatment conditions. Additionally, density functional theory (DFT) modeling was applied to reveal the active site and low energy reaction pathways at CuO(111) .

Results and discussion.

The main objective of this work was to study the correlation between structure/oxidation state and the active sites/phases of Cu-based catalyst. Both, reduced and oxidized catalyst show almost the same PROX activity and selectivity. According to DFT modeling, investigating O_2, CO, and H_2 adsorption on CuO(111), two pathways for CO and H_2 oxidation were suggested, as displayed in Fig. 1. The results show that Cu^+ prefers CO adsorption, Fig. 1(a), which is energetically favored over H_2 adsorption, Fig. 1(b), indicating that CO oxidation is thus preferred. The spontaneous consumption of lattice O confirms that the oxidation process proceeds *via* a Mars-van-Krevelen (MvK) mechanism, in line with literature.

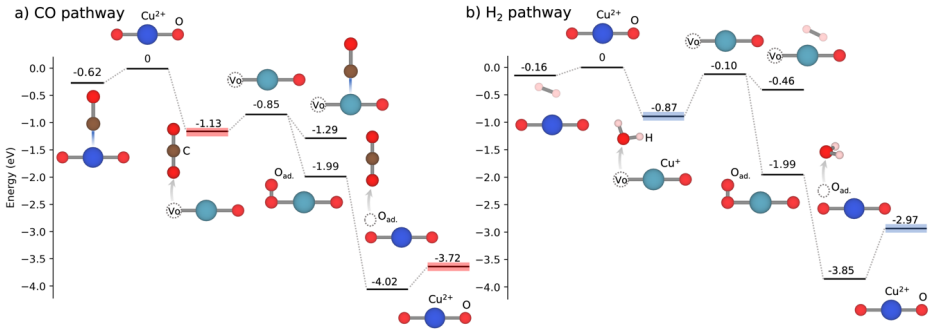

Fig. 1. a) CO and b) H_2 oxidation pathways on a CuO(111) surface.

Acknowledgments

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Atomic layer deposition for catalyst preparation: the zinc acetylacetonate reaction with mesoporous zirconia and alumina

J. Yim[1*], E. Haimi,[1] K. Meinander[1], P. Brüner[2],T. Grehl[2], A. Lempelto[3], L. Gell[3], T. Viinikainen[1], K. Honkala[3], R. Karinen[1], M. Putkonen[4], R.L. Puurunen[1]

[1]*Aalto University, Espoo, Finland*
[2]*IONTOF GmbH, Münster, Germany*
[3]*University of Jyväskylä, Jyväskylä, Finland*
[4]*University of Helsinki, Helsinki, Finland*

[*]*jihong.yim@aalto.fi*

Atomic layer deposition (ALD), a chemical vapor deposition process based on a sequential chemisorption of at least two reactants on solid surface, is an intriguing method for preparing heterogeneous catalysts with well-defined surface structures [1-2]. A recent study by Arandia et al. [3], related to this work, demonstrated the potential of zinc acetylacetonate [$Zn(acac)_2$] as an ALD reactant for tuning the surface properties of mesoporous metal oxide supports. Their study showed the beneficial effect of adding ZnO by ALD after the impregnation of copper on ZrO_2 for carbon dioxide hydrogenation into methanol [3]. Diethyl zinc (DEZ) is a well-known ALD zinc source. However, due to the pyrophoricity of DEZ, $Zn(acac)_2$ as a non-toxic reactant with a good thermal stability was regarded as an alternative option. This work focused on the details of ZnO ALD process used for catalyst preparation.

ZnO was added on mesoporous ZrO_2 (0.25-0.42 mm, BET surface area 54 m^2/g, median pore radius 8.3 nm) and Al_2O_3 particles (1.0 mm, BET surface area 158 m^2/g, median pore radius 4.6 nm) in a fixed bed ALD reactor. The ALD cycle was repeated up to three times for adding ZnO on ZrO_2. The $Zn(acac)_2$, which was vaporized at 120 ˚C, was chemisorbed on calcined supports at 200 ˚C for 3 h in the ALD reactor. The leftover acac ligands after the chemisorption were oxidatively removed in synthetic air in a tube furnace at 500 ˚C. Information on ZnO ALD on ZrO_2 was obtained by scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometry (EDS), inductively coupled plasma-optical emission spectrometry (ICP-OES), in-situ diffuse reflectance infrared Fourier transform spectroscopy-mass spectrometry (DRIFTS-MS), density functional theory (DFT) calculations, X-ray photoelectron spectroscopy (XPS), and low energy ion scattering (LEIS). ZnO ALD on Al_2O_3 was analysed by ICP-OES, SEM-EDS, and in-situ DRIFTS-MS.

The zinc loading after one ALD cycle on ZrO_2 saturated to ca. 1.3 wt% (2.2 Zn nm^{-2}) while increasing amount of $Zn(acac)_2$ was pulsed through support bed. Meanwhile, the zinc loading on Al_2O_3 with higher specific surface area kept increasing (highest measured: ca. 2.5 wt%). XPS and XANES analyses revealed that zinc existed as Zn^{2+}. By EDS analysis, zinc was observed throughout a ZrO_2 particle with slightly lower zinc intensity near the centre of the particle. Meanwhile, an eggshell-type ZnO coating was observed on Al_2O_3 particles. These results indicate that the reaction of $Zn(acac)_2$ most likely reached the saturation on the ZrO_2 surface and not yet on the Al_2O_3 surface. DRIFTS results showed that acac ligands adsorbed on ZrO_2 were removed as CO_2 up to 500 ˚C, while 100 ˚C higher temperature was needed to remove them on Al_2O_3. LEIS analysis showed that the surface of ZrO_2 was efficiently covered by atomically distributed ZnO after the first ALD cycle, acting as a nucleation center for subsequent ALD cycles.

Acknowledgments

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Tailoring ETL/ERI Zeolite Interfaces using Renewable Silica Source for Bio-Ethylene Production

K. Yomthong[1], N. Maineawklang[1], P. Iadrat[1], P. Pornsetmetakul[1], S. Ittisanronnachai[2] and C. Wattanakit[1*]

[1]*Department of Chemical and Biomolecular Engineering and School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand*
[2]*Frontier Research Center, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand*
** chularat.w@vistec.ac.th*

Keywords: Intergrowth of zeolite, Zeolite synthesis, ETL/ERI zeolites

Introduction. The hierarchical zeolite with intergrowth structures exhibited many advantages over pure-phase zeolites or physical mixtures in terms of catalytic, sorptive, or molecular separation properties.[1,2] However, the development of the well-defined zeolite with intergrowth structures is still in an early stage and it often suffers from the competition of phase separation of several metastable polymorphs.[2] In addition, phase competition led to defect generation, and these defects can promote a different crystalline structure formation, referred to as intergrowths.[3,4] Herein, we demonstrate the synthesis of intergrowth zeolite of unique ETL and ERI frameworks by using a renewable silica source. In addition, the structural evolution of interfaces in ETL/ERI intergrowth zeolites has been successfully obtained. Finally, the perspectives of catalytic activity using ETL/ERI intergrowth zeolites in bioethanol dehydration to ethylene have been demonstrated.

Experimental/methodology. Herein, ETL/ERI intergrowth zeolites were synthesized using starting gel composition of $2.0ChCl:0.3Rb_2O:0.7Na_2O:0.25Al_2O_3:5SiO_2:100H_2O$. The characterizations, including XRD patterns, SEM, and HRTEM images, and N_2 adsorption/desorption isotherms, were used for obtaining the morphological, textural, and structural properties. The NH_3-TPD and *in-situ* FTIR using pyridine as a probe molecule were used to determine acidic properties, which are crucial for the catalytic performance of bio-ethanol dehydration.

Results and discussion. The different forms of ETL zeolite were obtained using various silica sources under both dynamic and static crystallization processes. For example, the pure ETL zeolite is obtained using commercial colloidal silica (CSi), whereas changing silica sources to renewable nano-silica particles (NSP) results in the formation of the ETL/ERI intergrowth zeolite. The reason of the different phase formation relates to a different rate of hydrolysis and condensation between CSi and NSP. For example, in the static mode, the amorphous was obtained after 1 day of crystallization time (CT), while the crystalline ETL/ERI intergrowth zeolites were obtained after 2 days of CT when applying with NSP as a silica source. After prolonging the CT, a maximum ERI content (21 RC%) was obtained at 6 days of CT. A combination of XRD, TEM, and ED results confirms that ETL/ERI interfaces exist, possibly derived from competitive ETL and ERI crystal formation (**Figure 1**).[3,4] The designed intergrowth ETL/ERI zeolites show the high ethylene yield (xx %) from bioethanol dehydration, whereas this situation cannot be achieved when using the pure ERI. This work opens up the perspectives of intergrowth zeolites for catalytic applications.

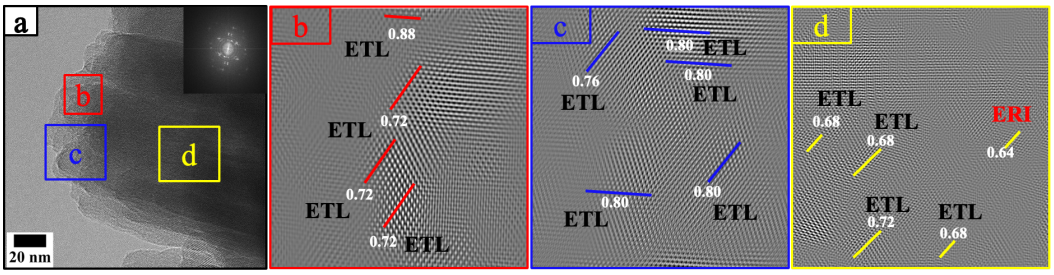

Figure 1. HR-TEM images of ETL/ERI intergrowth zeolite with respect to its Fast-Fourier Transform (a) and (b-d) the corresponding invert-FFT of the selected area images showing ETL and ERI phases.

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Synthesis of ordered carbonaceous frameworks with single-atomic metal species from octaethynyl metalloporphyrin

T. Yoshii[1]*, K. Chida[1], H. Nishihara[1,2], F. Tani[3]

[1] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan.*
[2] *Advanced Institute for Materials Research, Tohoku University, Sendai, Japan.*
[3] *Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, Japan.*
takeharu.yoshii.b3@tohoku.ac.jp

Keywords: Ordered carbonaceous frameworks, Single-atomic metal species, Electrocatalysis

Introduction. Ordered carbonaceous frameworks (OCFs) are a new class of carbon materials with a three-dimensional ordered structure synthesized by simple carbonization of metalloporphyrin crystals with polymerizable moieties (Fig. 1). Carbonization *via* solid-state polymerization results in the formation of graphene-based ordered frameworks, in which regularly aligned single-atomic metals are embedded with a content as high as 9 wt%. These unique structural features afford molecular-level designability like metal organic frameworks (MOFs) together with high electrical conductivity and thermal/chemical stability.[1-5] Herein, we focus on a new type of precursor, metalloporphyrin possessing eight ethynyl moieties (**6**) to produce highly porous OCFs towards a variety of catalytic applications.

Results and discussion. Ni-porphyrin with eight ethynyl moieties (**6**) has been employed as the precursor. Microporosity was developed during the carbonization process, and the resulting OCF shows the largest recorded S_{BET} of 673 m^2 g^{-1} in OCFs thus far. In addition, the OCF with well-developed porosity demonstrates a unique mechanical flexibility that enables force-driven reversible transition due to the structure composed of a non-stacked graphene sheet.[6] In addition, the extension of metal species in OCFs to Co, Cu and Fe has been succeeded using the same metalloporphyrin frameworks (**6**). XAFS analysis reveals the retention of M-N_4 coordination units without metal aggregation in the resulting M-OCFs (M; Ni, Co, Cu, and Fe) prepared at 600˚C. Furthermore, a bimolecular crystal can be yielded by simple mixing and recrystallization process to produce Co-Cu bimetallic OCFs. SEM-EDS and HAADF-STEM-EDS clearly indicate the homogeneous dispersion of single-site Co and Cu species without segregation in the resulting OCF.[7] A series of catalysts with various types of single-atomic metal species allow the systematic screen of the catalytic performance. In the presentation, the potential catalytic applications and further development of the OCF family will be discussed.

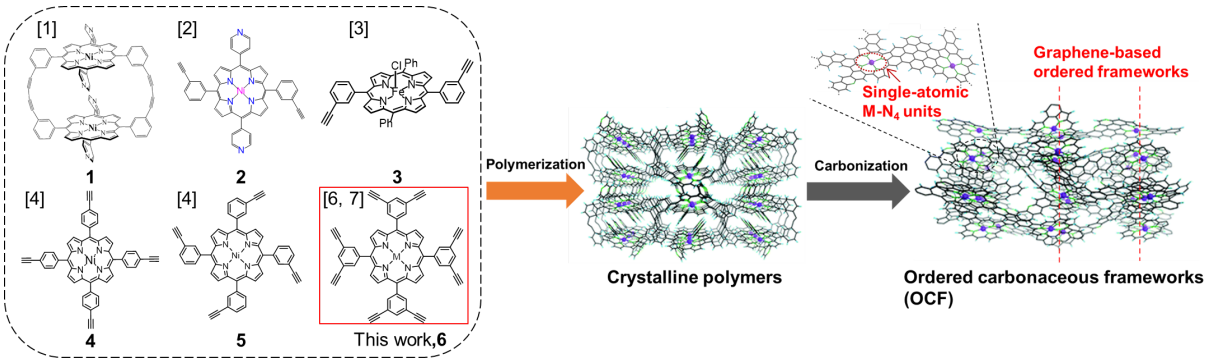

Fig. 1 Synthetic scheme of OCFs by the carbonization of metalloporphyrins (**1**-**6**).

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Selective Hydrogenation of Ethylene Carbonates over C_{60}-buffered Cu/SiO_2 under Mild Conditions

Yawen Mu, Xuelian Liang, Xufeng Liu, Jiachang Zuo, Jianwei Zheng, Su-yuan Xie, Youzhu Yuan*
State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols-Ethers-Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China
**E-mail: syxie@xmu.edu.cn; yzyuan@xmu.edu.cn*

Keywords: Ethylene carbonate, C_{60}-Cu/SiO_2, methanol, ethylene glycol, electronic buffer.

Introduction. The conversion and usage of CO_2 are of increasingly significance. The synthesis of ethylene carbonate (EC) from CO_2 and ethylene oxide, followed by further hydrogenation to produce methanol and ethylene glycol (EG), is a relatively mild and effective technique of using CO_2. The first-step reaction has been industrially applied at ambient pressure. However, the hydrogenation of ethylene carbonate requires elevated hydrogen (H_2) pressure (typically 2–3 MPa) and temperature (200 °C) over the catalysts such as Cu, Ni, and others. Further, the poor stability of the catalysts severely blocks the industrial application, which is more challenge in low-pressure systems.[1] Recently, we have discovered that fullerene (C_{60}) as an electron buffer can tremendously enhance the performance of Cu catalyst (C_{60}-Cu/SiO_2) for the hydrogenation of dimethyl oxalate to EG at ambient pressure.[2] Here, we report the new progress on the structure-performance of C_{60}-Cu/SiO_2 in selective hydrogenation of ECs.

Experimental/methodology. The *x*C_{60}-20%Cu/SiO_2 (*X* = 0, 5%, 10%, 15%, and 20%) catalysts were prepared by a urea-assisted gelation procedure.[2] Briefly, C_{60}, urea, $Cu(NO_3)_2 \cdot 3H_2O$, and 28 wt% aqueous ammonia, were dissolved in 100 mL deionized water to form a suspension. Then, 40 wt% Ludox AS-40 colloidal silica was slowly dropping under mechanical stirring. The suspension was vigorously stirred at 363 K in an oil bath for 4 h. The solids were washed, dried and calcinated to obtain final catalysts.

Results and discussion. Compared with the Cu/SiO_2 catalyst, the addition of C_{60} to Cu/SiO_2 showed different degrees of promotion effect, with the best one being 15 wt% C_{60} (Figure 1). At almost ambient pressure, no deactivation of the catalyst was seen after 250 h (Figure 2). This is primarily due to that the addition of C_{60} significantly promotes H_2 chemical adsorption and lowers the energy barrier for H_2 activation. Moreover, C_{60} can act as an electron buffer to regulate the valence state of Cu species, which benefits the activation of C–O bonds in ECs.[2] We further find that that Cu promotes the combustion of C_{60} in presence of air, and the phenomenon is observed more clearly by a thermogravimetric (TG) characterization in N_2 atmosphere. The available C_{60} content, which is defined as the proportion of C_{60} intimately contacted with the active Cu species by coordination, can be calculated by DTG curves measured in N_2 atmosphere (Figure 1). When this proportion is correlated with activity data, the results reveal the optimal coordination number of C_{60} in C_{60}-20%Cu/SiO_2. Therefore, the finding may be set as a preliminary parameter for estimating the catalyst activity of C_{60}-20%Cu/SiO_2.

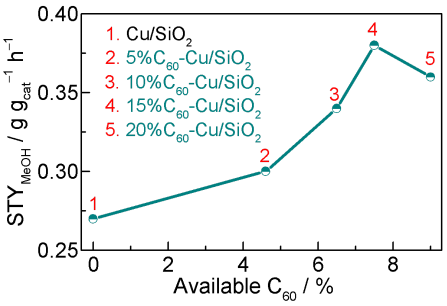

Figure 1. Catalytic performance of *x*C_{60}-20%Cu/SiO_2 samples with the different available C_{60} contents.

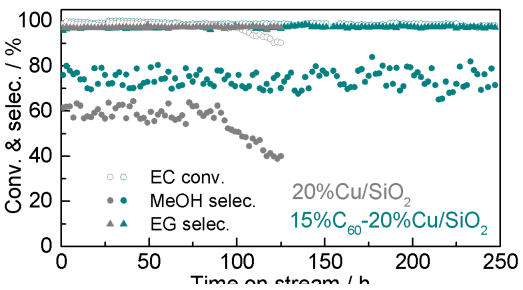

Figure 2. The stability tests in EC hydrogenation of Cu/SiO_2 and C_{60}-Cu/SiO_2 catalysts at 0.5 MPa and 453 K.

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Understanding the Effect of Polarity, Pt Particle Size, and Confinement on the selective hydrogenation of nitrostyrene.

M. Zaarour, J. Cazemier, F. Almukhtar, J.C. Navarro de Miguel, S. Komaty, J. Ruiz-Martinez*

King Abdullah University of Science and Technology, KAUST Catalysis Center (KCC), Catalysis Nanomaterials and Spectroscopy (CNS), Thuwal 23955, Saudi Arabia

** Corresponding author: javier.ruizmartinez@kaust.edu.sa*

Introduction. The selective hydrogenation of the NO_2 group in nitrostyrene over heterogeneous catalysts is challenging due to strong dependency of selectivity to several factors, for example to the metal nanoparticles (NPs) size and geometry, and the nature of the support. Herein, we propose an in-situ synthesis approach to confine and control the size of Pt NPs within a non-polar Silicalite-1 (S-1, MFI type zeolite) to obtain active and highly selective catalysts for the selective hydrogenation of the NO_2 group in 3-nitrostyrene.

Experimental. Pt was confined in S-1 through an in-situ encapsulation procedure where the Pt precursor is introduced in the synthesis gel, yielding Pt@S-1 with ~1.2 nm Pt NPs dispersed in the zeolite micropores. The selectivity is evaluated in the hydrogenation of 3-nitrostyrene (NS), nitrobenzene (NB), styrene (ST), NB and ST binary mixture, and ST hydrogenation in presence of aniline (AN). The role of confinement on selectivity is studied by comparing the performance of Pt@S-1 with the supported homologue Pt/S-1 with similar Pt particle size (1.9 nm Pt NPs). The role of host polarity is studied by comparing the non-polar Pt/S-1 with the polar Pt/SiO_2-2.2 bearing Pt NPs of similar size (2.2 nm) to Pt/S-1. Finally, the particle size effect is evaluated by comparing the catalyst Pt/SiO_2-2.2 with the commercial Pt/SiO_2-3.7 (3.7 nm Pt NPs).

Results and discussion. The Pt@S-1 confined catalyst demonstrates excellent selectivity to NO_2 hydrogenation in 3-nitrostyrene (70-80%), threefold higher than the commercial Pt/SiO_2-3.7, and this selectivity is more stable at high conversions than the supported Pt/S-1 (Fig. 1a). ST and NB competitive hydrogenation reveals the critical role of the host polarity in determining selectivity. The polar SiO_2 support enables the hydrogenation of both NB and ST, with higher activity in the C=C hydrogenation (Fig. 1d,e). The non-polar S-1 support on the other hand strongly suppresses ST hydrogenation and favors NB hydrogenation. This observation is further confirmed by DRIFTS adsorption experiments showing that ST could displace adsorbed NB and vice versa over the polar catalysts, meanwhile only NB could replace ST adsorbed on S-1 based catalysts. For catalysts with the same host, those with smaller Pt NPs are less active in C=C hydrogenation. Finally, very high ST conversion rates are obtained over SiO_2-based catalysts in presence of AN (Fig. 1f), similar to those obtained for ST hydrogenation in the absence of NB (Fig. 1c); meanwhile it was much lower over the confined Pt@S-1 and affected to a lesser extent over Pt/S-1 suggesting the preferential adsorption of AN versus ST on the S-1 based catalysts.

In summary, the high NO_2 selectivity over Pt@S-1 in the hydrogenation of NS and NB + ST binary mixtures is explained by the lower C=C hydrogenation activity due to the decreased polarity of S-1 compared to SiO_2 on the one hand, and the smaller Pt NPs than the external Pt/S-1 due to size constraints imposed by confinement, on the other hand. The selectivity is further enhanced by AN adsorption on Pt@S-1 that decreases the efficiency to ST adsorption and hydrogenation compared to individual ST hydrogenation (Fig. 1c), thus explaining the stable selectivity at high conversions.

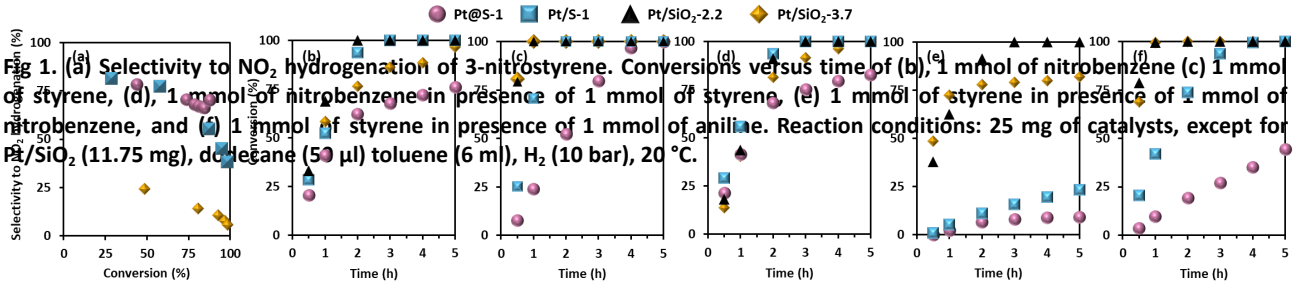

Fig 1. (a) Selectivity to NO_2 hydrogenation of 3-nitrostyrene. Conversions versus time of (b), 1 mmol of nitrobenzene (c) 1 mmol of styrene, (d), 1 mmol of nitrobenzene in presence of 1 mmol of styrene, (e) 1 mmol of styrene in presence of 1 mmol of nitrobenzene, and (f) 1 mmol of styrene in presence of 1 mmol of aniline. Reaction conditions: 25 mg of catalysts, except for Pt/SiO_2 (11.75 mg), dodecane (50 µl) toluene (6 ml), H_2 (10 bar), 20 °C.

Determination of the mechanism of poisoning the catalytic surface with chlorine originating from the support precursor

M. Zakrzewski[1*], O. Shtyka[1], J. Rogowski[1], R. Ciesielski[1], A. Kedziora[1] and T. Maniecki[1]

[1]*Department of Chemistry, Institute of General and Ecological Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland*

[*]*mateusz.zakrzewski@p.lodz.pl*

Keywords: residual chlorine; methane reforming; mechanism; poisoning

Introduction. There are many reasons for the deactivation of catalytic systems. This can be caused by carbon deposits, sintering, or poisoning of the active surface. Many catalyst poisons e.g. phosphine, arsenic compounds, sulfur compounds, and chlorine block active surfaces. The aim of the work was to investigate and determine the mechanism of poisoning of catalytic systems with chlorine originating from the decomposition of the support precursor.

Experimental/methodology. The 20%Ni/5%La_2O_3-95%Al_2O_3 catalyst used in the study of the catalytic mechanism of surface poisoning was prepared in three stages. Initially, the Al_2O_3 support was obtained by precipitation using ammonia as a precipitating agent to obtain a pH of the solution in the range of 9-10. Then, the Al_2O_3 compound was used to obtain the La_2O_3-Al_2O_3 system using the wet impregnation preparation method. The nominal loading of La_2O_3 was 5%. Finally, the prepared oxide system was impregnated with nickel. The nominal metal content in the obtained catalyst was 20%.

The obtained catalytic system was subjected to physicochemical tests: X-ray diffraction (XRD), Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), Temperature-Programmed surface reaction, and tests of catalytic activity in the mixed methane reforming (MRM) process. The volume ratio of the reaction reagents in each test was as follows: CH_4:CO_2:H_2:H_2O:Ar = 2:2:1:0.9:1.25 [1].

Results and discussion. In this work, the influence of the catalytic support precursor on the activity of the nickel catalyst in the mixed methane reforming process was investigated. TPSR tests carried out in a helium atmosphere showed that in the temperature range of 25 – 900 °C chlorine is removed from the system in the form of hydrogen chloride. However, this process is not 100% efficient. The use of TOF-SIMS analysis showed that the catalyst prepared with lanthanum (III) chloride after the reduction process showed significant chlorine poisoning of the system (Figure 1). Finally, the catalytic activity tests showed that the activity of this system is lower than the catalyst prepared with the use of lanthanum (III) nitrate (V) precursor (Table 1). The result of this work is the proposed mechanism of surface chlorine poisoning from the catalytic precursor.

Table 1. CH_4 and CO_2 conversions for monometallic catalyst system prepared from nitrate and chloride support precursor.

Catalytic system /Support precursor	Conversion of CH_4 after 3h reaction	Conv of aft reaction
20%Ni/5%La_2O_3-95%Al_2O_3 / Lanthanum (III) nitrate (V)	71%	68%
20%Ni/5%La_2O_3-95%Al_2O_3 / Lanthanum (III) chloride (V)	49%	56%

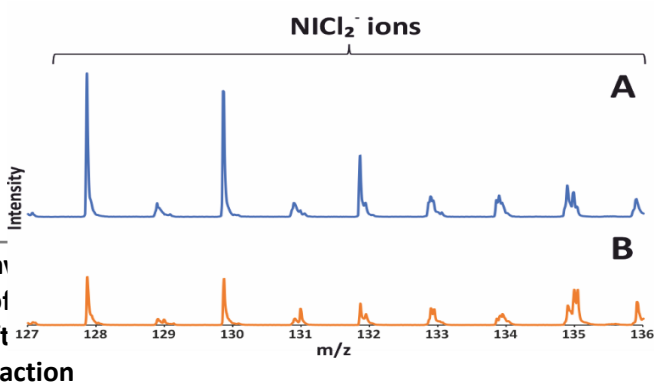

Figure 1. TOF–SIMS spectra of the 20%Ni/5%La_2O_3–95%Al_2O_3 catalyst (after

reduction (A) and (B) after calcination) presenting peaks of $NiCl_2^-$ ions.

Acknowledgments

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Catalyst design for the direct reforming of crude oil into hydrogen

D. Zapater*, M. Albuali, M. Alamro, X. Yao, N. Morlanes, J. Gascon, P. Castaño

KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955−6900, Saudi Arabia
**diego.zapaterbes@kaust.edu.sa*

Keywords: Hydrogen, crude oil, crude−to−hydrogen , reforming.

Introduction

Hydrogen demand has increased by around a 50 % since the beginning of the century due to the global growth of essential chemicals production and rising environmental requirements. The petrochemical industry is the leading consumer of hydrogen because it is necessary for a wide range of products. In this industry, ammonia (66 %) and methanol (22 %) are the main targeted products [1]. The one−step crude−to−hydrogen process is a promising route to obtain hydrogen directly from converting crude oil. This process can be carried out by steam (SR) or autothermal (ATR) reforming [2]. The crude−to−hydrogen process is interesting because it allows for obtaining hydrogen directly and it can take advantage of the existing infrastructure and know−how of refineries.

This work proved that crude−to−hydrogen is a promising alternative for hydrogen production directly from crude oil. We tested this process on a laboratory scale for several feeds of crude oil and catalytic technologies and with a preliminary cost analysis study with the current market values.

Experimental/methodology

Several catalysts were prepared following various methods and charecterized by different techniques. The feed of mixed water and crude oil was a liquid (emulsion) or a gas−liquid (liquid crude oil pushed by steam). A HPLC pump controlled the feed of this mixture (water−to−oil w/o mass ratio= 6), to a packed bed reactor at W/F_{Crude}= 40 $g_{cat} \cdot g_{crude}^{-1}$ min^{-1}, 800 ^{0}C, and 1 bar, using a 15 wt. % of N_2 as carrier and internal pattern. The collection of condensable products (*e.g.* water and heavy hydrocarbons) was a condensator operating at 10 ^{0}C. These products were mainly water (>95 wt. %) and no further analyisis was performed over them. Non−condensable products were analyzed by an online GC. Coke formed in the catalyst was obtained from difference between initial and final mass of catalyst. The average mass balance was greater than 86 % for all catalytic tests.

Results and discussion

Handling crude oil and water mixtures is a complex matter that we addressed by two ways. The first one was preparing emulsions with different w/o ratios that behave as non−Newtonian fluids but are stable. However, reaction results showed that their evaporation was uneven, causing pressure increase and making it unfeasible to operate. The second way was by pushing crude oil with steam. This way provided uniform evaporation and stable pressure for longer. Reaction results showed different performances for the tested catalyst. These resuslts can be correlated with catalysts properties, such as structure or metal content, and reaction conditions. In the best case, we achieved a maximum of 80 mol. % of hydrogen in the gas product stream and 14 h of uninterrupted operation. Our simulations showed that SR produces more hydrogen, but its energy costs are more significant, while ATR has a lower hydrogen production but has lower (and even close to zero) external energy demand. Because the needed equipment and infrastructure is the same as in any current refinery, the economic viability of the process depends mainly on the prices of the raw materials. Hydrogen production cost ($\$ \cdot kg^{-1}$) by crude−to−hydrogen is lower than that of natural gas SR when crude is below 40 $\$ \cdot bbl^{-1}$ and natural gas is above 8 $\$ \cdot MMbtu^{-1}$.

Acknowledgments
Funding for this work was provided by King Abdullah University of Science and Technology (KAUST)

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Enhanced oxygen reduction reaction activity of $BaCe_{0.2}Fe_{0.8}O_{3-\delta}$ cathode for proton-conducting solid oxide fuel cells via Pr-doping

Xin Zhou, Jian Zhang, Yicheng Zhao* ,Yongdan Li[2]

[1]*Department of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, China*
[2]*Department of Chemical and Metallurgical Engineering, Aalto University, Kemistintie 1, FI-00076 Aalto, Finland*
**E-mail for Yicheng Zhao: zhaoyicheng@tju.edu.cn*

Keywords: Proton-conducting solid oxide fuel cell, Praseodymium doping Barium ferrite, Oxygen surface exchange.

Introduction. Under the global energy shortage and environmental pollution, solid oxide fuel cells (SOFCs), as efficient and clean power generation devices with wide fuel flexibility, have received extensive attention in recent years [1]. At a lower temperature, the cathode polarization dominates the cell loss of PCFCs [2]. Therefore, developing highly active cathode materials for PCFCs has become a research focus. Among the existing cobalt-free PCFC cathodes, mixed ionic-electronic conducting $BaFeO_{3-\delta}$-based materials have been widely studied considering the low price, and good chemical stability. In recent years, Pr has been used as a dopant in electrode materials of SOFCs. In this work, Pr is partially substituted for Fe in $BaCe_{0.2}Fe_{0.8}O_{3-\delta}$ as a cathode material for PCFCs. The effects of the Pr-doping on the surface property and oxygen surface exchange kinetics are studied.

Experimental/methodology. Cathode powders of $BaCe_{0.2}Fe_{0.8}O_{3-\delta}$, $BaCe_{0.2}Fe_{0.7}Pr_{0.1}O_{3-\delta}$, $BaCe_{0.2}Fe_{0.6}Pr_{0.2}O_{3-\delta}$ and $BaCe_{0.2}Fe_{0.5}Pr_{0.3}O_{3-\delta}$were synthesized through an EDTA-citrate sol-gel method [3]. Stoichiometric $Ba(NO_3)_2$, $Fe(NO3)_3 \bullet 9H_2O$, $Ce(NO_3)_3 \bullet 6H_2O$and $Pr(NO_3)_3 \bullet 6H_2O$ were dissolved in deionized water at 60 °C. Then citric acid and EDTA were added to the aqueous solution at a molar ratio of 1:1:1.5 for total metal ions: EDTA: citric acid. The solution was stirred at 90 °C until a yellow gel was formed, which was subsequently heated to 350 °C for 2 h, and then calcined at 1000 °C for 5 h. $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ electrolyte was prepared through a solid-state reaction method [4]. The anode substrate and the BZCY electrolyte powders were co-pressed at 300 MPa and then calcined at 1350 °C for 5 h. The cathode slurry was screen-printed on the electrolyte layer, followed by calcination at 950 °C in air for 3 h.

Results and discussion. The cathode is composed of a cubic $BaFeO_{3-\delta}$ phase and an orthorhombic $BaCeO_{3-\delta}$ phase, and Pr is doped in both phases. The partial substitution of Pr for Fe decreases the content of the $BaFeO_{3-\delta}$ phase, leading to lower electrical conductivity. $BaCe_{0.2}Fe_{0.6}Pr_{0.2}O_{3-\delta}$ has the most adsorbed oxygen and Fe^{3+} on the surface, resulting in the fastest oxygen surface exchange kinetics and the highest activity. The partial pressure of H_2O shows a negligible effect on the polarization resistance of the cathode. In contrast, the polarization resistance increases remarkably with the decrease of oxygen partial pressure, indicating that the rate of the cathode process is controlled by the surface exchange of oxygen. At 700 °C, $BaCe_{0.2}Fe_{0.6}Pr_{0.2}O_{3-\delta}$ shows the lowest polarization resistance of 0.057 Ω cm^2, and a single cell with that cathode exhibits the highest maximum power density of 562 mW cm^{-2}.

Acknowledgments

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Boosting of metal-support interactions between Ru with sodium titanate nanowire on the hydrogenolysis of polyolefins under mild conditions

Xueping Zhang[1], Guo-Ping Lu[1]

[1]*School of Chemistry and Chemical Engineering, Nanjing University of Science & Technology, Xiaolingwei 200, Nanjing 210094, China*

[*]*Corresponding Author's E-mail address: glu@njust.edu.cn*

Keywords: hydrogenolysis of polyolefins, metal-support interaction, Ru nanoparticles, sodium titanate nanowires, liquid alkanes

Introduction. Polyolefin is the most widely used plastic, accounting for about 57% of the total plastic in the world [1], and its non-degradable properties make the recycling of plastic waste the most important link in "plastic control" [2]. The catalytic hydrogenolysis of polyolefins has attracted wide attention because of its relatively mild reaction conditions, good reaction activity and good product selectivity. Therefore, it is of great practical significance to explore the catalysts for hydrogenolysis of polyolefins. Ru, as one of the most active metals in the hydrogenolysis of polyolefins with C-C bond, provides an excellent choice for the hydrogenolysis of polyolefins [3]. It has been found that the support type has a great influence on the performance of Ru catalysts for hydrogenolysis of polyolefins. Herein, we explore a Ru catalyst supported on sodium titanate nanowires for hydrogenolysis of polyolefins.

Experimental/methodology. In the synthesis process of Ru/NTO-NH, sodium titanate nanowires (NTO) were first prepared by hydrothermal stirring approach, Ru was loaded on NTO by impregnation reduction approach, and the metal-support interaction (MSI) was adjusted by changing the calcination process parameters. In addition, the Ru/NTO-NH catalyst has better catalytic performance than general Ru/TiO_2 catalyst. Under the reaction conditions of 180 °C, 1 MPa H_2, and 8 h, it can effectively convert low-density polyethylene (LDPE) to high selective hydrogenolysis to high value liquid alkanes.

Results and discussion. In this work, a series of novel NTO supported Ru catalysts have been developed, in which significant MSI between Ru and NTO are observed. Ru/NTO-NH has stronger MSI than other Ru catalysts, which is attributed to sequential N2 calcination and H2 reduction. The improved MSI of Ru/NTO-NH is conducive to the formation of smaller, more positively charged and NTO coated Ru NPs, which results in higher H coverage rate and weaker alkane adsorption capacity. Therefore, this catalyst is beneficial to the hydrogenolysis of LDPE internal C-C bonds under mild conditions (180 oC, 1 MPa), leading to full conversion and high selectivity to liquid alkanes (88%). The hydrogenolysis of other polyolefin plastics including HDPE, PP, LDPE plastic bags can be also achieved by Ru/NTO-NH with good conversion and selectivity. It also exhibits excellent stability and recyclability, and no significant activity degradation is observed after 10 runs.

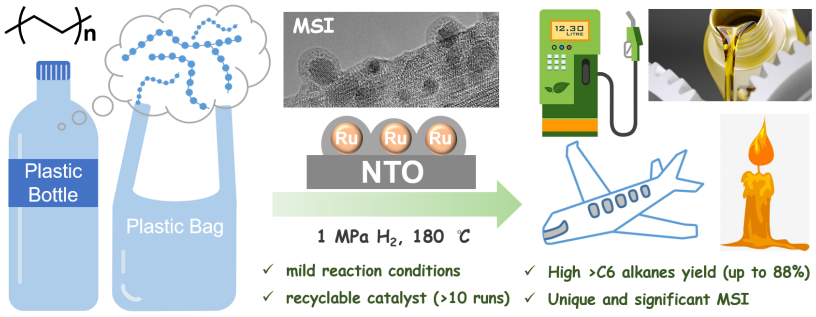

Figure 1. Catalytic application of Ru/NTO-NH catalyst in hydrogenolysis of plastics.

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Palladium supported onto organo-functionalized halloysite nanotubes as catalyst for hydrogenation reactions

S. Bedoya[1,*], C.C Torrez[2], C. Herrera[1], C.H Campos[1]

[1]*Universidad de Concepción, Concepción, Chile*
[2]*Universidad Andres Bello, Sede Concepción, Talcahuano, Chile*
sanbedoya@udec.cl

Keywords: Catalytic hydrogenation, Nitrobenzene, Furfural, Halloysite.

Introduction: Noble metal (NM) mediated catalytic hydrogenation is an important topic in the chemical industry, which provides a clean and environmentally friendly strategy to produce highly valued commodities. However, the high cost and scarcity of NMs has limited their use or scalability. The use of NM nanoparticles (NPs) confined to the inner surface of nanotubes has emerged as an attractive methodology to achieve this goal [1]. One interesting material for this purpose are halloysite nanotubes (HNT), which have an alumina inner wall and a silica outer wall [2]. Selective functionalization of the inner surface of HNT could provide metal NP-based catalysts with significant efficiency and operational stability. On this way, this contribution is aimed in the synthesis and catalytic evaluation of Pd nanoparticles supported onto the inner surface of organo-modified halloysite to provide highly efficient and operational stable catalysts for the hydrogenation of two kind of molecules: (1) nitrobenzene (NB) to produce aniline (AN) as model reaction for the production of amines of pharmaceutical interest and (2) furfural (FUR) to produce 2-methyl furane (2MF) or tetrahydrofurfuryl alcohol (THFOL) as model reaction for biomass valorization [3].

Experimental/methodology. The halloysite nanotubes were pre-treated by pyrolysis at 400°C. Then, the inner surface was organo-functionalized by contacting the halloysite with dopamine hydrochloride (DOPA) in ethanol (DOPA/HNT = 0.01 mass ratio) in an Ar atmosphere. The deposition of the Pd NPs was carried out using a methanolic solution of palladium (II) chloride precursor, which was contacted with the organo-functionalized nanotubes and dried in vacuum to obtain the final solid. Different palladium metal loadings 0.25, 0.50, 1.0 and 2.0% (w/w%) were evaluated. The solids were pyrolyzed and reduced with H_2. The obtained catalysts were characterized by the following techniques: TGA, NMR, ICP-MS, H_2-Chemisorption, XRD, Nitrogen adsorption isotherm, SEM-EDAX, TEM and XPS. The catalytic activity of the catalyst was evaluated in NB as well as FUR hydrogenation using ethanol or dodecane as solvents, respectively, at 30°C and 10 bar of H_2 pressure for NB and 120°C and 20 bar of H_2 for FUR, with constant magnetic stirring. The reactions were quantified using GC-FID.

Results and discussion. The physicochemical characterization of the Pd supported catalyst displayed that the HNT-DOPA surface area decrease after the DOPA immobilization. In addition, TGA show that the organic content on the support was similar to the nominal loading value. In addition, the H_2-chemosorption indicate a decrease of the metal dispersion with the increase of metal content. The XPS analysis showed $Pd^{\delta+}$ surface species, which increased with the increase of the metal loading. All the catalyst showed good catalytic performance, for NB and FUR hydrogenation, that fitted to a pseudo-first kinetic model and a high selectivity to the desired AN or THFOL products, respectively. Among them, the 0.5Pd/HNT-DOPA catalyst show the higher catalytic efficiency. Furthermore, this catalyst displayed the optimal operational stability reaching 5 recycles remaining a high conversion and selectivity to the AN and THFOL products, respectively.

Acknowledgments
The authors thanks Agencia Nacional de Investigación y Desarrollo (ANID) FONDECYT Project 1231352 and 1231395. S. Bedoya thanks to University of Concepción EDPG program for his doctoral scholarship.

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Ru Nanoparticles Immobilized on Guanidinium-Based Supported Ionic Liquids Phases as Adaptive Hydrogenation Catalysts

Yuyan Zhang,[1] Liqun Kang,[1] Serena DeBeer,[1] Alexis Bordet,[1*] Walter Leitner [1,2*]

[1] *Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany*

[2] *Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Germany.*

**Corresponding Author's E-mail address: alexis.bordet@cec.mpg.de / walter.leitner@cec.mpg.de*

Introduction. Adaptive catalytic systems are capable of adjusting their performance in response to changes in their environment, and are thus attracting increasing attention to cope with the dynamics associated with the use of renewable resources (intermittent energy supply, variations in feedstock quality, etc.).[1-2] Recently, our group reported the immobilization of Ru nanoparticles (NPs) on a CO_2-responsive tertiary amine-functionalized polymer-grafted silica support (PGS).[1] The resulting multifunctional catalytic system was applied to the hydrogenation of ketone-containing furan derivatives, and responded adaptively to the feed gas composition (full hydrogenation under H_2, no ketone hydrogenation under H_2/CO_2). In this case, the Ru-catalyzed reversible formation of ammonium formate species by reaction of CO_2 and H_2 at the amine-functionalized support was identified as trigger for the selectivity switch. While this catalyst was demonstrated to be fully adaptive, the complex polymeric structure and the heat treatment required to decompose the ammonium formate and regenerate the original activity of Ru NPs were identified as limitations.

Experimental/methodology. In this context, we propose here an alternative catalyst design in which Ru NPs are immobilized on a simple guanidinium-based supported ionic liquids phase (SILP) (Figure 1a).[3] The prepared Ru@SILP material was characterized by a combination of techniques including electron microscopy, solid state NMR, and X-ray absorption spectroscopy. While ammonium formate species cannot form through CO_2 hydrogenation with such catalyst structure, we hypothesize that the guanidinium IL-like environment may stabilize formic acid sufficiently for it to act directly as a trigger to switch selectivity.

Results and discussion. The Ru@SILP catalyst was applied to the hydrogenation of biomass-derived furfuralacetone (**1**) as a model reaction. Full hydrogenation to the saturated alcohol **2** was observed under pure H_2, as expected for Ru NPs. In contrast, the C=O hydrogenation activity was shut down under H_2/CO_2, and the saturated ketone **3** was obtained. Satisfyingly, the selectivity switch was found fully reversible and products **2** and **3** were produced alternatively in high yield and selectivity simply by changing the composition of the feed gas between H_2 and H_2/CO_2 (Figure 1b). Detailed investigations and characterizations showed that the Ru-catalyzed reversible formation of formic acid by CO_2 hydrogenation act as trigger for the selectivity switch. Such selectivity switch was not observed using Ru@SiO_2 or imidazolium-based Ru@SILP catalysts, and the guanidinium IL environment was found essential to reach a concentration of formic acid high enough to enable adaptivity.

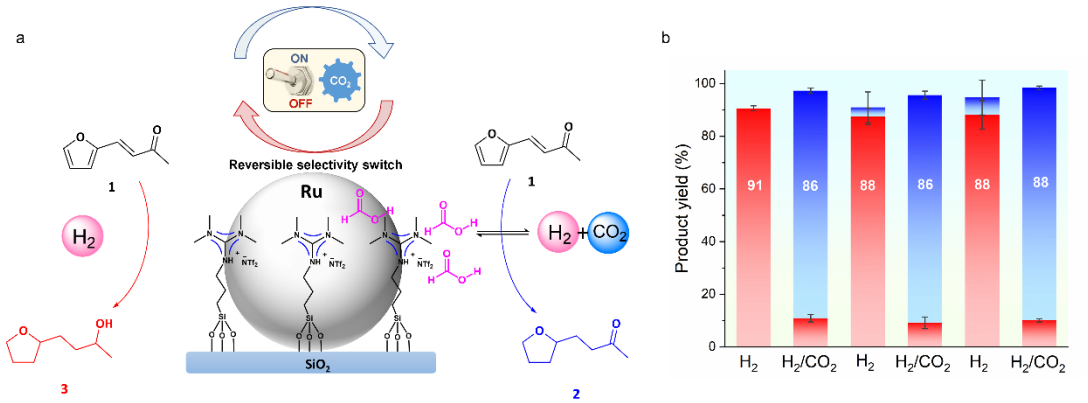

Figure 1. (a) Hydrogenation of furfuralacetone under H_2 or H_2/CO_2 as feed gas. (b) Reversibility study, reaction conditions: Ru@SILP (0.005 mmol), furfuralacetone (50 eq., 0.25 mmol), 1,4-dioxane (0.65 mL), H_2 (15 bar) or H_2/CO_2 (45 bar, 1:2), 80°C, 16 h, red-yield of **3**, blue-yield of **2**.

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Modification of zeolite confinement by extra-framework clusters promoting alkane cracking

R. Zhao[1], R. Khare[1], Y. Zhang[1], M. Sanchez-Sanchez[1], R. Bermejo-Deval[1], Y. Liu[1,*], J. A. Lercher[1,*]

[1]*Technical University of Munich, Garching, Germany*
[*]*johannes.lercher@ch.tum.de*

Keywords: Zeolite, Confinement, Extra-framework alumina, Extra-framework silica, alkane cracking

Introduction. Catalytic active sites in zeolites are constituted by both the bridging SiOHAl groups that act as Brønsted acid sites (BAS) and by surrounding microporous cavities that solvate confined species involved in catalytic cycles[1]. Both the cavity framework and extra-framework species afford such constraint and solvation and influence catalytic reactions[2, 3]. The presence of extra-framework alumina (EFAl) in proximity of a BAS enhances its catalytic activity in n-pentane cracking by 50 folds. Extra-framework silica (EFSi) is another type of extra-lattice species, however its role in catalytic reactions is hitherto unidentified. Here we controllably create EFSi in the vicinity of BAS ion MFI zeolite, and show the different mechanisms for the enhancement of catalytic activity in protolytic cracking of n-pentane in comparison to that of EFAl.

Experimental/methodology. Parent H-MFI zeolite was obtained by dealuminating on a commercial H-MFI (CBV 2314 from Zeolist) with ammonia hexafluorosilicate and further calcination at 773K. EFAl was created by controllable steaming of the parent H-MFI. EFSi was grafted into H-MFI by adsorbing n,n-dimethyltrimethylsilylamine and calcined at 773K for 5h.

Results and discussion. The presence of EFAl or EFSi in H-MFI makes a portion of BAS with nearby EFAl or EFSi. In order to differ from normal BAS, they are denoted as EFAl-BAS or EFSi-BAS. The turnover frequencies (TOFs, rate normalized to total BAS) for overall cracking, dehydrogenation and different cracking pathways of n-pentane reaction on MFI zeolites all show linear increase with the portion of EFAl-BAS or EFSi-BAS in the total BAS (Figure 1). By extraploting TOFs to 100%, the TOF of all reaction pathways were obtained for EFAl-BAS and EFSi-BAS. As shown in Figure 2, the TOF on EFAl-BAS is 50-fold higher than normal BAS. This significant of enhancement was attributed to the higher transition entropy, overcompensating the increase of the activation energy. However, on EFSi-BAS, the increment of TOF was only 2-fold higher. This enhancement was attributed to the lower activation energy.

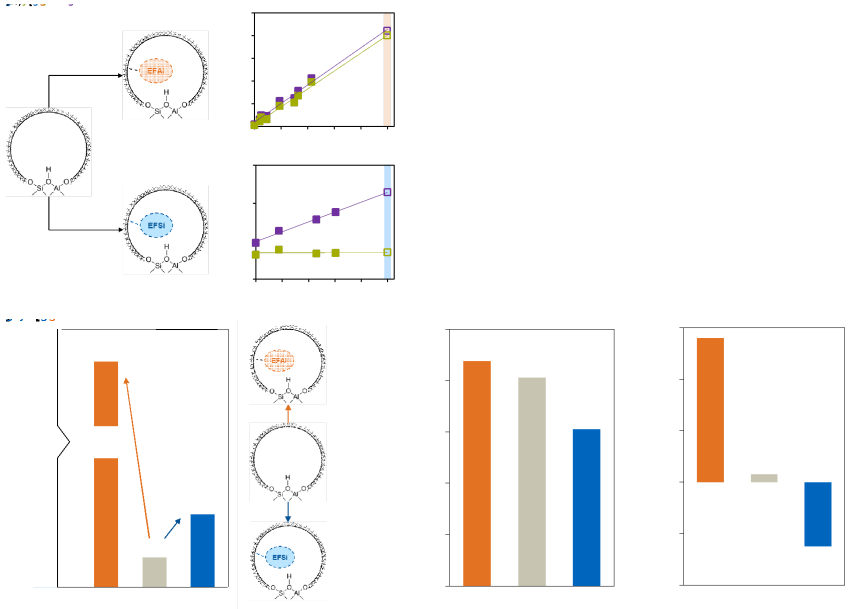

Figure 2. The influence of EFAl and EFSi on the TOF (753 K), intrinsic activation enthalpy and entropy for n-pentane cracking on H-MFI zeolites.

Conceptual work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), Division of Chemical Sciences, Geosciences and Biosciences (Transdisciplinary Approaches to Realize

Novel Catalytic Pathways to Energy Carriers, FWP 47319). R. Z. is grateful to the Chinese Scholarship Council for the financial support. The authors also acknowledge M. Iqbal and M. Neukamm for the technical support concerning nitrogen physisorption and the elemental analysis, respectively.

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MOF-Triggered Synthesis of Subnanometer Ag^0_2 Clusters and Fe^{3+} Single Atoms: Heterogenization Led to Efficient and Synergetic One-pot Catalytic Reactions

Y. Zheng*, C. Bilanin, J. Oliver-Meseguer, M. Mon, A. Leyva-Pérez

Instituto de Tecnología Química, Universitat Politècnica de València–Consejo Superior de Investigaciones Científicas (UPV-CSIC), Valencia, Spain
**yzheng3@itq.upv.com*

Keywords: MOFs, Ag clusters, oxidative cross-coupling, styrenes, sulfones, phenylacetylenes, one pot.

Introduction. The direct catalyst conversion of alkenes to alkynes is an unmet synthetic pathway with high potential impact in organic synthesis.[1] Alkynes are pluripotential building blocks for organic synthesis, which engage in a multitude of reactions such as hydrogenation, hydroaddition, cross–coupling, metathesis and pericyclic reactions. However, alkynes are generally expensive and difficult to implement in kilogram studies since their synthesis often relies on highly energetic intermediates. In this contribution we will show how the synthesis of different metal species in well-defined solid catalyst has allowed to carry out the challenging direct conversion of styrenes to phenylacetylenes in one pot.[2]

Experimental/methodology. First of all, the reaction was carried out using different homogeneous catalysts. Then, a metal–organic framework (MOF), in particular $Fe^{3+}Ag^0_2$@MOF, was synthesized in order to perform the reaction with a heterogeneous catalyst. Once the reaction parameters were optimized, the reaction mechanism was studied using different techniques. Finally, the reaction scope was done with many compounds.

Results and discussion. The solid $Fe^{3+}Ag^0_2$@MOF is capable of catalyzing the oxidative cross-coupling of styrenes with phenyl sulfone, to give vinyl sulfones in yields up to >99%. Vinyl sulfones can be transformed, in situ, to the corresponding phenylacetylene products in high yields, after filtration of the catalyst, which can be reused.

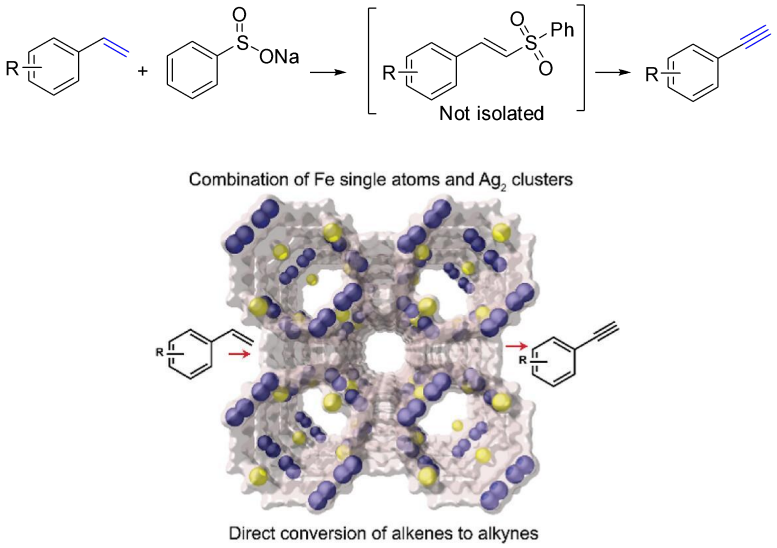

Figure 1: Reaction scheme for the formation of alkynes from alkenes.

Acknowledgments

Y.Z. thanks to the China Scholarship Council (CSC No: 202009350009) for a Ph.D.Fellowship. C.B. thanks ITQ for a contract. M.M. and J.O.–M. acknowledge MICIIN from a contract under the Juan de la Cierva program (FJC2019–040523–I, and IJC2018–036514–I, respectively). Thanks to MICINN (Spain, Project TED2021-130465B-I00).

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Different Dimensions of Carbon Materials for Supercapacitors

Shuang Zong[1,2], Aibing Chen[1], Xinying Liu[2*]

[1] *College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, 70 Yuhua Road, Shijiazhuang 050018, China.*

[2]*Institute for the Development of Energy for African Sustainability (IDEAS), University of South Africa (UNISA), Florida Science Campus, Private Bag X6, Johannesburg 1710, South Africa.*

Email: liux@unisa.ac.za, +86-0722868656.

Keywords: Carbon nanospheres, carbon nanotubes, carbon nanosheets, supercapacitor

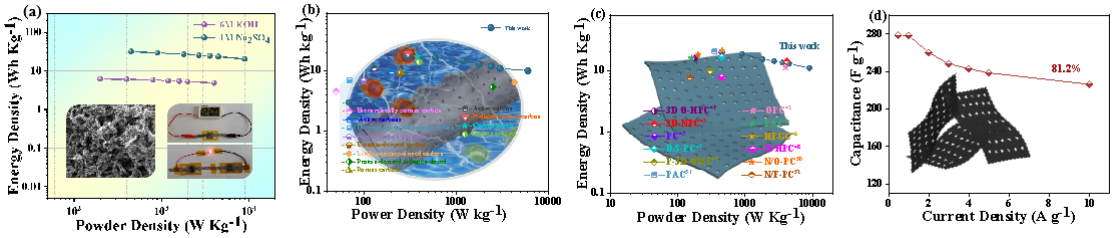
Introduction

As a type of energy storage device that falls somewhere between traditional capacitors and batteries, the supercapacitor has the advantages of energy saving and environmental protection, high power density, fast charging speed, long cycle life, etc.[1, 2] One of the key factors affecting the performance of the supercapacitor is the electrode material, and carbon nanomaterials are the most widely studied and applied electrode materials for supercapacitor[3]. Carbon nanotubes/nanofibers with a one-dimensional (1D) structure have a relatively regular pore structure, a large specific surface area (SSA), high conductivity and chemical stability [4]. Carbon nanosheets with a 2D structure have a large SSA, high electrical conductivity, and stable thermal and chemical properties [5]. Herein, we synthesized carbon materials with different dimensions as electrodes for supercapacitor. We were systematically investigated the electrocatalytic performance of these carbon materials and the relationship between their structure and performance.

Experimental/methodology

The following methodology was adopted: silica assisted strategy, template co-assembly method for carbon nanofibers and carbon nanotubes; Interfacial self-assembly guide strategy for carbon nanosheets.

Results and discussion



(a) Hierarchically porous carbon nanofibers with tunable morphology and outstanding capacitive performance. (b) Ragone plots for the carbon nanotube symmetric supercapacitors. (c) Ragone plots for the carbon nanosheets symmetric supercapacitor. (d) Rate performance of the porous carbon nanosheets.

Acknowledgments

We thank the Natural Science Foundation of Hebei (B02020208088), the S&T Program of Hebei (20544401D, 20314401D, 206Z4406G, B2021208074), and the Tianjin Science and Technology Project (19YFSLQY00070).

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Recovery of gold from melted boraxes with simultaneous production of pure BF3 Catalyst, also suitable for doping Silicon for semiconductors and Graphene

Author's Name : T. Zucca[1*]

[1]*Industrial and Civil Engineering Professional Office Ing. Tullia Zucca, Comazzo, Italy*

[*]*Corresponding Author's E-mail address : info@gandzsas.com*

Keywords: keyword 1 : Gold Recovery in mining and industrial electronic wastes, keyword 2 : BF3 pure Catalist , keyword 3 : Doping Silicon for semiconductors and Graphene

Introduction. The invention belongs to a continuously expanding field, given that precious metals are no longer used only in the production of jewels and luxury items, but are increasingly used in electronic devices which are increasingly used throughout the world. More, this invention produces pure BF3, an important Catalist , fitted for a lot of process: Friedel - Crafts acylation and alkylation reactions . These reactions are not exactly catalytic, since BF_3 is consumed. For example:

$$PhH + RX + BF_3 \rightarrow Ph\text{-}R + H^+ + BF_3X^-$$

More :polymerization reactions of unsaturated compounds such as alkenes .isomerization reactions of saturated and unsaturated hydrocarbons, cracking of hydrocarbons in the oil industry, esterification and condensation reactions, synthesis of other boron compounds such as boranes and borates, synthesis of lubricant additives, P-type doping in the manufacture of semiconductors , doping of both silicon and graphene.

Untill now BF3 has been produced in different way, but never so pure as our new process is able to obtain.

Experimental/methodology: The granulated borax lavas , derived from precious metal castings in mines or from disused electronic devices, containing Gold , is dispersed in the whole mass of the reagent, aqueous solution of hydrofluoric acid with a titre of 40% of HF in H2O .

The solid/liquid slurry immediately enters the chemical reactor, which can also be a common reactor which is slightly stirred and with a fixed vent for the gaseous reaction product, but which in our plants will preferably be represented by the controlled cavitation machine, a special construction for this Process, given that hydrofluoric acid has the ability to attack very strongly the normal construction materials of chemical plants.

To respect the reaction times, the slurry is recycled in a loop on the machine, but it is also possible to recycle it in a large loop on the static mixer, in case it is necessary to add another reagent, up to the optimal stationary reaction regime.

The adoption of our controlled cavitation machine will certainly make the process more efficient by reducing reaction times and minimizing energy consumption, which however in the process in question is in itself very low, making this new process very convenient also from this point of view.

The end of the reaction and therefore the release of all the gold that was occluded in the solidified borax matrix after melting, is easy to prove, as it occurs that the gaseous flow of boron trifluoride , the reaction product, gas already at 12°C under the atmospheric reaction conditions, which is continuously vented and bubbled in a container partially filled with diethyl ether , which is brought to the titre up to 46% of boron trifluoride etherate . Boron trifluoride can be absorbed in other chemical compounds, such as Toluene, Methanol or other Chemicals. In any case it is advisable to store the boron trifluoride absorbed in diethyl ether or other chemical , at a very widespread catalyst, in various fields, its marketability is therefore high. We specify that this by-product synthesized by us is purer than those already on the market, obtained by other methods.

Results and discussion . BF3 , direct product of the chemical reaction, should not be considered a by-product of the process, even if the main product is considered to be recovered gold, because it has very important uses. Gold recovery and simultaneous production of BF3, is a really milestone in updated technologies.

H_2 and carbon production through Fe-catalyzed methane decomposition

I. Giarnieri[1], E. Gioria[2], A. Bertuzzi[1,2], V. Foderà[3], A. Bobitan[4], N. Omori[4], G. Fornasari[1], S. D. M. Jacques[4], M. C. Righi[3], A. M. Beale[4], C. Damsgaard[2], P. Benito[1,*]

[1]*Dept. Industrial Chemistry "Toso Montanari", University of Bologna, Bologna, Italy*
[2]*National Centre for Nano Fabrication and Characterization, Technical University of Denmark, Lyngby, Denmark*
[3]*Dept. Physics and Astronomi "Augusto Righi", University of Bologna, Bologna, Italy*
[4]*Finden Limited, Merchant House, Abingdon, UK*
[*]*patricia.benito3@unibo.it*

Keywords: H_2, methane decomposition, Carbon Nanotube.

Introduction. H_2 will play a key role in the decarbonisation to reach a reduction of GHG of 55% by 2030 and the net zero emissions by 2050 and in the REPowerEU Plan [1]. Green H_2 obatined by water electrolysis uisng renewable energy will be the main contributor in the H_2 economy; nevertheless, other solutions are searched to bridge the gap between the conventional steam methane reforming (grey H_2) and water electrolysis. Catalytic decomposition (or cracking) of methane (CDM) is a valuable COx-free hydrogen production technology [2]. The added-value is the production of carbon materials for special applications. However, the key advantage of the methane cracking, the production of solid carbon, also provokes the catalyst deactivaiton and clogging of the reactor, hence hampering the process implementation. Herein we present the work in progress within the framework of the Horizon Europe STORMING project to obtain low cost catalysts for the production of H_2 and carbon nanotubes (CNTs) [3]. Fe-based catalysts are developed by a combination of theoretical (Density Functional Theory, DFT) and experimental methodologies with the aim of increasing the catalyst lifetime and controlling the properties of the CNTs.

Experimental/methodology. Catalysts are synthetized by co-precipitation and calcination. The Fe loading, composition of the oxide matrix (e.g. Al_2O_3 or spinel) and presence of promoters are modified, also following the inputs given by DFT. A screening of the catalysts and reaction conditions (temperature, composition of the feedstock, and GHSV) is performed in a fixed-bed quartz reactor. The characterization of the fresh and spent catalysts, including the carbonaceous deposits, is performed by XRD, H_2-TPR, micro-Raman, SEM and TEM.

Results and discussion. The selective production of H_2 through the methane decomposition at tempeartures below 800 °C is feasible over the Fe-based catalysts investigated. The H_2 productivity and the properties of the carbonaceous materials, e.g. degree of crystallinity and morphology, are largely dependent on both the type of catalyst (Fe loading and support) and reaction conditions. For instance, carbon fibers are produced with high loaded Fe/Al_2O_3 catalysts. Besides the composition of the catalyst, its activation procedure and the GHSV are key parameters to be tailored to increase the catalyst lifetime and to obtain CNTs with controlled properties.

Acknowledgments
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Effect of the internal wettability of catalyst supports on gas-production reactions: study of H_2O_2 decomposition

F.D. Bernal Juan[1*], A. Banerjee[1], L. Lefferts[1]

[1] *Catalytic Processes and Materials Group, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands*
[*] *f.d.bernaljuan@utwente.nl*

Keywords: wettability, catalyst support, bubble evolution, mass transfer, effective kinetics

Despite the relevance of the formation of gas bubbles in multiphase catalytic reactions, the number of studies that address this issue is limited. It has been shown that bubbles influence mass and heat transport [1,2]. For example, bubbles detaching from a catalyst particle surface, or moving inside the pore network, can enhance mass transfer [2,3]. But it's also true that bubbles covering the catalytic surface can also hamper the diffusion of reactants, thus limiting the reaction. Within our research group we have shown that it is possible to manipulate the external and internal wettability of a catalyst support [4,5]. These studies show that it is possible to enhance the transport of chemical species present in the gas phase in a three-phase reactor. However, the understanding of how the internal wettability of this new type of support influences bubble formation or movement in gas-evolving reactions is lacking. In this study, we use as a model system to shed some light on these matters the catalytic decomposition of H_2O_2 (eq. 1) in aqueous solution on hydrophilic and partially hydrophobic catalysts supports (Pt/Al_2O_3). This catalytic reaction is simple but we have observed that it is possible to readily fall under internal mass transfer limitations.

$$2H_2O_2 \xrightarrow{cat} 2H_2O + O_2 \qquad (1)$$

A series of supported catalysts with increasing hydrophobicity have been synthesized as reported earlier by physically mixing powders of hydrophilic and hydrophobic alumina [4]. The prepared catalysts were tested in a batch reactor under stirring, and the reaction rate is calculated by measuring the oxygen evolution rate. The described experimental setup allowed the determination of mass transfer effectiveness factors varying the stirring speed and H_2O_2 concentration. This is significant as this allows the comparison of the Thiele's pore effectiveness factor with experimental data, and determine the effect of bubbles forming due to the catalytic reaction.

Acknowledgments
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Tuning the catalytic activity of supported non-noble metal nanoparticles in oxidation reactions of aliphatic alcohols

Chiara Bersani,[1] Alvise Perosa,[1] Daily Rodríguez-Padrón, [1] and Maurizio Selva*[1]
[1]*Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari di Venezia, 30123 Venezia, Italy*

*selva@unive.it

Keywords: green chemistry, catalysts design, supported nanoparticles, non-noble metal catalysts, selective oxidation reactions

Introduction. The fundamental role of hetergeneous catalysis in the chemical industry has raised in recent years, looking forward the design of more environmentally-friendly processes which be compatible with the sustainable development goals.[1] In this context, the synthesis of efficient, selective, stable and low-cost catalytic materials is a highly pursued objetive.[2] Considering the aforementioned premises, through this contribution, the preparation of a series of carbon-supported non-noble metal nanoparticles was accomplished via a sustaineble strategy and their catalytic activity was investigated in the oxidation of aliphatic alcohols, being able to tune the products distributions by controlling the reaction conditions.

Experimental/methodology. The catalytic materials were prepared following a two-step protocol based on an impregnation step of the biomass-derived carbon source with the selected non-noble metal precursors and a subsequent thermal treatment. The materials were fully characterized following a multitechnique approach and their catalytic activity was tested in the oxidation of 1-hexanol (as model aliphatic alcohol). Furthermore, a substrate scope investigation was carried out considering primary and secondary alcohols.

Results and discussion. This contribution aimed at the design of a sustainable methodology for the preparation of selective catalytic materials. It is worth to highlight that a biomass-derived feedstock was employed as carbon source and that the synthetic strategy allowed the formation of homogeneous and well-dispersed non-noble metal nanoparticles, as confirmed from TEM-analysis. The catalytic oxidation of 1-hexanol was studied employing the prepared catalytic samples, leading to a remarkable outcome in particular for molybdenum-based systems. Moreover, the most efficient catalytic material was used to perform a full parametric analysis and subsequently a substrate scope investigation was accomplished under the optimized conditions. As well, it was possible to stablish a relationship between the catalytic performance and the textural, morphological and chemical features of the samples. Finally, the materials displayed an outstanding reusability for, with negligible loss of the catalytic activity along 5 reaction cycles.

Acknowledgments
C.B. thanks the support from Fondazione Cariplo (Photo- and Mechano-Chemistry for the Upgrading of Agro- and Sea-food Waste to advanced polymers and nanocarbon materials, CUBWAM, project 2021-0751)

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Design and Development of CO Methanation Catalysts for a Novel Coal to SNG Production Technology

B. Acar[1,2], B. S. Çağlayan[2,3], A. E. Aksoylu[1,2*]

[1]*Department of Chemical Engineering, Boğaziçi University, Bebek, Istanbul 34342, Turkey*
[2]*SNG&HydTec Lab, Science and Technology Building, Boğaziçi University, Kandilli, Istanbul 34684, Turkey*
[3]*Advanced Technologies R&D Center, Boğaziçi University, Bebek, Istanbul 34342, Turkey*
[*]*aksoylu@boun.edu.tr*

Keywords: CO Methanation, Synthetic Natural Gas, CH_4 Production

Introduction. Owing to uneven and limited distribution of the natural gas reserves and the concerns about the rising greenhouse gas emissions, industrial and academic studies have focused on the production of synthetic natural gas (SNG)[1]. The current work is a part of the ongoing project conducted in our SNG&HydTec Lab that ultimately aims the design and development of industrial catalysts for a novel, economically feasible, coal to SNG production technology. The main purpose of this particular work is to design and develop novel methanation catalyst(s) having high methane production activity and selectivity with performance stability allowing efficient methane production even for feeds having H_2:CO<3 through combining CO methanation with WGS reaction.

Experimental/methodology. A series of Ni based methanation catalysts were designed and prepared. In preparation, types of metals, promoters, supports, metal loadings, pretreatment conditions were used as experimental parameters. The performance of the catalysts was determined experimentally in ranges of 200-400 °C, under both ideal flow (ie. feeds having H_2:CO=3) and realistic flow conditions (feeds having H_2:CO<3, including CO_2, steam, etc).

Results and discussion. Figure 1 shows the CO conversion values at three different feed compositons and at two different temperatures for 16 different catalyts. At 400 °C, for H_2:CO=3, all catalysts, except 5%Ce 10%Ni/ZrO_2, showed similar CO conversion performances (93 to 98%). When H_2/CO ratio was decreased to 2, CO conversion values were not obviously changed for most of the catalysts. However, when the H_2:CO ratio was lowered to 1, both CO conversion and CH_4 yield values decreased. Comparison of CO conversion results obtained at low temperatures indicates more significant differences between catalyst performance. For example, at 250 °C, only 6 of the 16 catalysts show CO conversion performances even with ideal H_2:CO feed ratio of 3. Moreover, 5%Ce-10%Ni/γ-Al_2O_3 is the only catalyst that works at 250 °C for H_2:CO=2 with good catalytical activity and stability.

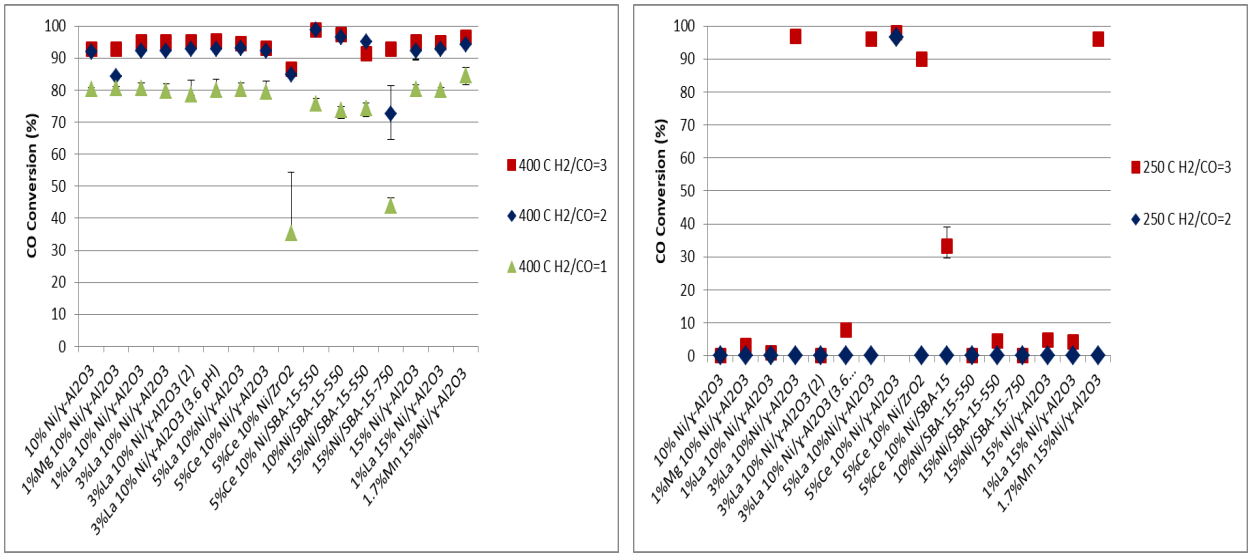

Figure 1. CO Conversions for different H_2/CO ratios at 400 °C (a), at 250 °C (b)

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Novel versatile covalent phenyl-BTBT-based triazine extended as metal-free heterogeneous photocatalyst

M.Carmen Borrallo-Aniceto[1*], Mercedes Pintado-Sierra[2], Félix Sánchez[2], Marta Iglesias[1]
[1]*Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid 28049, Spain*
[2] *Instituto de Química Orgánica General, CSIC, Madrid 28006, Spain*
[*]*mcarmen.b@csic.es*

Introduction. Polymers based on covalent triazine networks (CTFs) are a class of porous organic polymers (POPs) characterized by excellent chemical and thermal stability, large specific surface areas, well-defined microporosity, and high nitrogen content [1].
The combination of triazine units (acceptor groups) with donor groups (aromatic groups) in a conjugated structure makes CTFs excellent candidates for use in photocatalytic reactions [2,3].
Thus, in this work, we have prepared a CTF-based polymer using a novel dinitrile monomer based on the semiconducting benzo[b]benzo[4,5]thieno[2,3-d]thiophene (BTBT) core with extended conjugation through phenyl units for its applications in oxidation reactions, Diels-Alder and halogenations.

Experimental/methodology. In this work, a triazine with BTBT skeleton has been successfully prepared. The synthesis of the monomer has been carried out in three steps: First, 2-chlorobenzaldehyde is reacted with NaHS, followed by bromination at positions 2 and 7. This is followed by Suzuki-Miyaura cross-coupling using 4-cyanophenylboronic acid to extend the BTBT moiety with additional phenyl rings.
The synthesis of the catalyst is performed by microwave activation using trifluoromethanesulfonic acid obtaining CTF in quantitative yield, which is insoluble in water and in all common organic solvents.

Results and discussion. To confirm that the monomer is part of the polymeric network we have performed 13C CP/MAS NMR in solid state, and the thermogravimetric analysis (TGA) curves showed that the polymer has a good thermal stability (Td= 560ºC) (figure 1). The photocatalyst was evaluated in different reactions such as selective oxidation reactions (sulfides to sulfoxides, hidroxilation), Diels-Alder reactions and halogenations with excellent conversions (100%) and yields (>98%) using 5 mol% catalyst (figure 2).

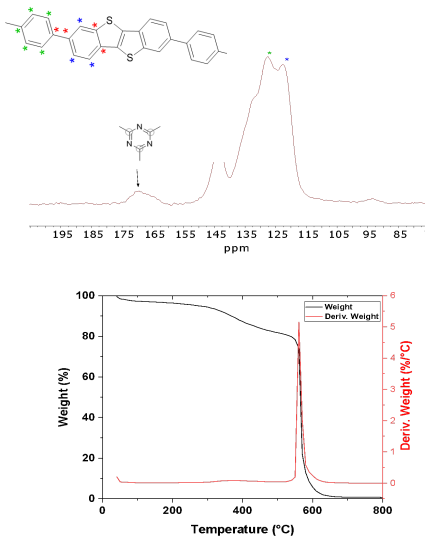

Figure 1. ^{13}C-NMR solid state (up) and TGA of phenyl BTBT based CTF (down)

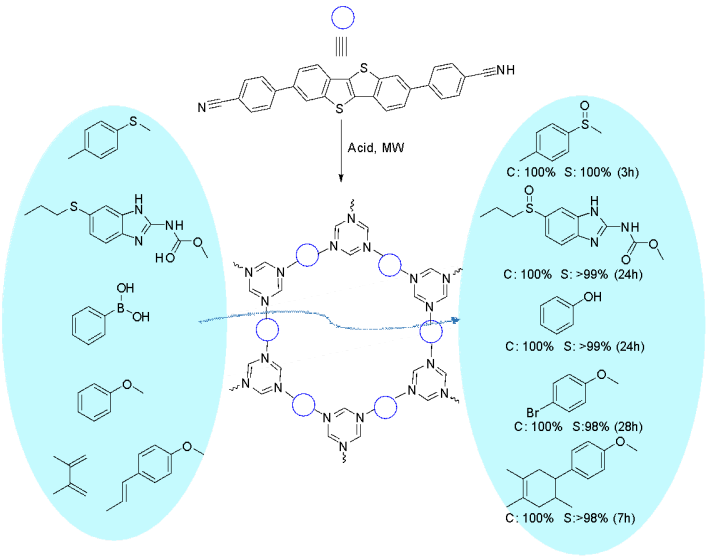

Figure 2. Schematic representation of the phenyl-BTBT based CTF and the reactions used

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Ru nanocatalysts for sunlight-powered methanation of CO_2: distinguishing between photothermal and non-thermal contributions

D. Burova[1,2,3,*] , J. Rohlfs[4], F. Sastre[4] , M. Xu[4], P. Martínez Molina[4], N. Meulendijks[4] , M. A. Verheijen[5,6] , A.-S. Kelchtermans[1,2,3], K. Elen[1,2,3], A. Hardy[1,2,3], M. K. Van Bael[1,2,3], P. Buskens[1,4]

[1] *Institute for Materials Research, DESINe, Hasselt University, Diepenbeek, Belgium*
[2]*IMEC VZW, IMOMEC Associated Laboratory, Diepenbeek, Belgium*
[3]*EnergyVille, Genk, Belgium*
[4]*The Netherlands Organisation for Applied Scientific Research (TNO), Eindhoven, The Netherlands*
[5]*Department of Applied Physics, Eindhoven University of Technology, Eindhoven, The Netherlands*
[6]*Eurofins Materials Science, Eindhoven, The Netherlands*
[*] *Correspondence: daria.burova@uhasselt.be*

Keywords: CCU; surface plasmon resonance; photocatalysis; *in operando* monitoring; Sabatier reaction

Introduction. Two major challenges that we as society currently face are securing our future energy supply by switching from fossil fuels to sustainable energy sources, and reducing CO_2 emissions. CCU techniques are aimed at capturing CO_2 and putting it to good use. A promising CCU technique is the chemical conversion of CO_2 to CH_4, which is a safe and easy-to-handle energy carrier with a high gravimetric storage density. Conventionally, the Sabatier process ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) catalyzed by supported metal nanoparticles such as Ni, Rh and Ru requires activation at temperatures between 300°C and 500°C. Here, we present SiO_2 and Al_2O_3-supported Ru nanocatalysts tailored for use of sunlight as energy source instead of conventional heating. Using mildly concentrated sunlight as sole energy source (up to 6.66 $kW \cdot m^{-2}$) and supported Ru nanocatalysts of a size between 0.8 nm and 3.4 nm, we achieved a methane production rate up to 0.63 $mol \cdot g_{Ru}^{-1} \cdot h^{-1}$ at ≥ 99% selectivity and a catalyst bed temperature of 220°C.[1] To distinguish between photothermal and non-thermal contributions, which is of interest both from a fundamental and application perspective, we monitored the temperature at the surface and inside the catalyst bed *in operando* using a tailored optical sensor, which to date has only been demonstrated offline.[2]

Experimental/methodology. Two different methods were used for decoration of the supports, viz. γ-Al_2O_3 and Stöber SiO_2, with Ru nanoparticles: (1) deposition-precipitation followed by chemical reduction (CR) using $RuCl_3$ as a precursor, and (2) impregnation with $Ru_3(CO)_{12}$ and subsequent high-temperature decomposition (TD).[1] The chemical composition of the prepared catalysts, their nanostructure and optical characteristics - UV-vis-NIR reflectance, skin depth and emissivity – were studied in detail. To distinguish between photothermal heating and potential non-thermal contributors, e.g. transfer of hot electrons to an electron-accepting orbital of an adsorbate in close proximity, a single thermocouple measurement of the catalyst bed temperature does not suffice. Instead, accurate *in operando* temperature monitoring of the catalyst bed is required. For that purpose, we applied fiber Bragg grating based fiber optic temperature sensors.[2] By positioning multiple sensors at various depths, we were able to accurately monitor not only the top surface temperature during the reaction, but also quantify temperature gradients.

Results and discussion. The Ru nanoparticles in Ru/γ-Al_2O_3-CR were slightly larger than in Ru/γ-Al_2O_3-TD (1.2 vs. 0.8 nm). In addition, Ru nanoparticles were deposited on Stöber SiO_2 using both deposition techniques. Ru/SiO_2 particles were larger than the ones deposited on γ-Al_2O_3 (2.5 and 3.4 nm for CR and TD, respectively). Taking into account the size differences between the Ru nanoparticles, all catalysts displayed similar activity (0.14–0.63 $mol \cdot g_{Ru}^{-1} \cdot h^{-1}$) and selectivity (≥99%) in the sunlight-powered Sabatier reaction. We monitored the temperature of the catalyst bed during the reaction as function of the sunlight intensity, the flow rate and the feedstock composition to differentiate between photothermal and non-thermal contributors to the sunlight-powered CO_2 methanation

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Pre-defining the surface environment of the Ti species in Mg/Ti Ziegler-Natta catalysts for polypropylene

F.D. Cannavacciuolo[1,4*], G. Antinucci[1,4], R. Cipullo[1,4], V. Busico[1,4], M. Khoshsefat[2,4], T. Toshiaki[2,4], L. Falivene[3,4], L. Cavallo[3,4]

[1]*Department of Chemical Sciences, University of Naples Federico II, Naples, Italy*
[2]*Japan Advanced Institute of Science and Technology, Ishikawa, Japan*
[3]*King Abdullah University of Science and Technology, Thuwal, Saudi Arabia*
[4]*Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, the Netherlands*
[*]*feliciadaniela.cannavacciuolo@unina.it*

Introduction.

Ziegler-Natta catalysts for the production of isotactic polypropylene are formulations in which $TiCl_4$ and an organic Lewis base ('Internal Donor', ID) are co-adsorbed on a nanostructured $MgCl_2$ support; this solid precatalytic phase is subsequently contacted with an AlR_3 activator, usually complexed with another organic Lewis base ('External Donor', ED) [1,2]. Under polymerization conditions, some IDs react with the AlR_3 and desorb from $MgCl_2$ surface [3]; in this case the action of active site modification is dominated by the ED [2,4]. No attempts to purposely modulate ID/AlR_3 reaction kinetics and, therefore, to control the distributions of catalytic species and of relevant polymer properties thereof have been reported so far. In the proposed research approach, we have integrated a state-of-the-art high-throughput experimentation (HTE) workflow and fast computational tools to investigate the question systematically.

Experimental/methodology.

Studies of the ID/AlR_3 reactivity in solution and on the surface ($MgCl_2$/ID model adducts) were performed using a Freeslate Extended Core Module (XCM™) robotic platform [5]. $MgCl_2$/ID/$TiCl_4$ precatalysts were tested in propene homopolymerization with a Freeslate Parallel Pressure Reactor (PPR48) platform [6], and the produced polymers were characterized by means of Rapid-Gel Permeation Chromatography (GPC), Analytical Crystallization Elution Fractionation (ACEF) and ^{13}C NMR all used in HTE mode. All molecules were manipulated on GaussView[7] and all the calculations run on Gaussian 16.[8]

Results and discussion.

A robust dataset of ID/$AlEt_3$ reactivities in solution was built-up using a training library of 22 molecules. For the investigated IDs, all featuring carbonyl moieties, carbonyl reduction in solution turned out to follow a single well-defined kinetic law; in addition, the apparent specific rate (k_{app}) values nicely populated the desired modulation range (i.e., k_{app} values between those of reference dibutylphthalate and diisobutylsuccinate). Unexpectedly, ID/$AlEt_3$ reactivities following ID chemisorption onto $MgCl_2$ turned out to be rather insensitive to individual ID structures, which likely indicates strong surface-specific effects. In addition, catalyst modification by a known competent ED resulted into substantial enhancements of stereoselectivity and molecular weight capability (which in most systems closely approached the levels of a reference dibutylphthalate-containing system), but not into a broadening of the molecular weight distributions. A multiple regression Quantitative Structure-Property Relationship (QSPR) model was implemented to rationalize ID surface reactivity with $AlEt_3$. Using a Machine Learning approach for features selection, a satisfactory QSPR equation was obtained with 2 steric and 3 electronic descriptors (using suitably selected catalyst features).

Acknowledgments

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Enhanced hydrocinnamaldehyde selectivity through support and geometric effects by encapsulation of platinum in S-1

J. Cazemier[1], M. Zaarour[1], P. Lavrik[1], S. Veeranmaril[1], S. Komaty[1], A. Aguilar[2], J. Ruiz-Martinez[1]*

[1]*King Abdullah University of Science and Technology, KAUST Catalysis Center (KCC), Catalysis Nanomaterials and Spectroscopy (CNS), Thuwal 23955, Saudi Arabia*

[2]*The European Radiation Synchrotron Facility, 71 Avenue des Martyrs, 38043 Grenoble, France*

** Corresponding author: javier.ruizmartinez@kaust.edu.sa*

Introduction. The chemoselective hydrogenation of the C=C bond in cinnamaldehyde (CAL) to obtain hydrocinnamaldehyde (HCAL) remains challenging over Pt-based heterogeneous catalysts. Reported catalysts are often complex and selectivity remains below 90%. Herein, we report selectivities of 99% by utilizing Pt NPs encapsulated in Silicalite-1 zeolite for improved support effects and smaller Pt NPs.

Experimental/methodology. Pt was encapsulated in S-1 through an in-situ encapsulation procedure where the Pt precursor is introduced to the synthesis gel, yielding Pt@S-1 with 0.8 nm Pt NPs dispersed in the zeolite micropores. The selectivity in the hydrogenation of cinnamaldehyde was evaluated at 100°C and 10 bar H_2 in toluene. The support effect was investigated by comparing Pt/S-1-ex and Pt/SiO_2-ex, which were prepared by impregnating colloidal Pt NPs possessing Pt NPs size exclusively on the surface of Silicalite-1 and SiO_2, respectively. Particle size effect was investigated by comparing Pt@S-1 with Pt/S-1-ex and encapsulated catalysts with different particle sizes prepared through in-situ encapsulation or incipient-wetness impregnation. The catalyst properties were further characterized by CO chemisorption followed by DRIFTS, and the spent catalysts were analyzed by STEM.

Results and discussion. The confined catalyst, Pt@S-1-in, achieved 99% HCAL selectivity at 78% CAL conversion (fig. 1a), significantly higher than a commercial Pt/SiO_2 (85%) at similar conversion level (74%). The reasons for such high selectivity were thoroughly investigated. Catalysts with the same Pt particle size but different supports (fumed SiO_2 versus silicalite-1) revealed that the support polarity plays a significant role in enhancing selectivity (fig 1a,b). Catalysts with lower silanol density and thus decreased polarity show significantly improved HCAL selectivity. However, the selectivity of Pt/S-1-ex shows a rapid decrease in selectivity at higher conversions, not observed in encapsulated catalysts. The subsequent analysis of spent catalysts revealed that catalysts suffer from some sintering under reaction conditions, however, the encapsulated catalysts maintain the smallest particle size. The onset of hydrocinnamyl alcohol formation appears to be correlated with the particle size. The catalyst with the largest particle size (Pt/S-1-ex, fig. 1c), and thus the most detrimental Pt(111) facets, forms HCOL early in the reaction whereas the catalyst with the smallest Pt particles (Pt@S-1-in, fig. 1d) presumably only forms HCOL after some sintering has occurred.

In summary we have demonstrated that Pt@S-1 enhances the HCAL selectivity, achieving the highest reported selectivity for Pt-based catalysts. The selectivity is due to the reduced polarity of the S-1 support, but there is a noticeable enhancement due to the confinement which restricts the size of the Pt NPs.

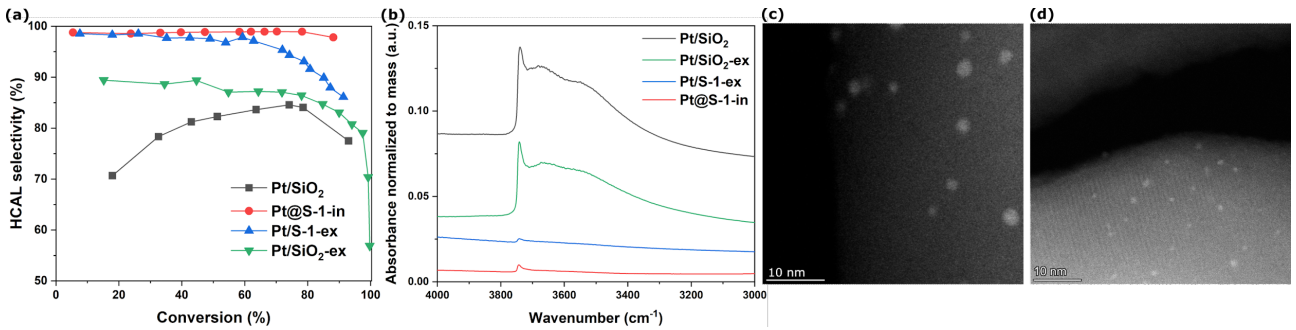

Figure 1. (a) CAL conversion vs HCAL selectivity. Reaction conditions: CAL (300 mg), Pt (1 mg), H_2 (10 bar), toluene (6 ml), 100°C. (b) Silanol region of the FTIR spectrum for catalysts. Representative HAADF-STEM image of (c) Pt/S-1-ex and (d) Pt@S-1-in.

ZrO_2/NH_2-SiO_2 bifunctional flow microreactor for deacetalization-Knoevenagel domino process

A. Ciemięga[1*], K. Maresz[1], J. Mrowiec-Białoń[1]

[1] *Institute of Chemical Engineering Polish Academy of Sciences, Gliwice, Poland*
([*]ciemiega@iich.gliwice.pl)

Keywords: domino process, microreactors, silica monolith

Introduction. Domino reactions involve two or more consecutive reactions leading to the final product without addition of any new substrates, with no intermediates` isolation and employing one fixed workup procedure. This methodology, used for the formation of complex molecules, was evolved for biologically important natural substances, agrochemicals and pharmaceuticals production. One of the challenges in this area is to elaborate catalysts with functionalities which are able to cohabitate and act cooperatively or independently [1].

In this work, the benefits of micro-flow technology and bifunctional heterogeneous catalysis were combined. Silica monolithic cores of microreactors were functionalized with both acid (zirconia) and base (amine) active groups. Microeactors were tested in the deacetalization – Knoevenagel condensation domino process.

Experimental/methodology. Silica monoliths of hierarchical pore structure were modified with zirconium isopropoxide and propylamine or polyamine precursors. Chemical and structural characteristics were obtained using FTIR, thermogravimetry and nitrogen sorption analysis. Catalytic experiments were performed in the flow regime. The synthesis of ethyl α-cyanocinnamate was carried out using benzaldehyde dimethyl acetal and ethyl cyanoacetate as substrates. Catalytic experiments were conducted in: i) microreactor doped with ZrO_2, ii) microreactor with amine group and iii) bifunctionalized microreactor. The performance of microreactors modified with different amine centers was compared.

Results and discussion. Monolithic silica was successfully functionalized with both acid and base sites which was confirmed by TG and FTIR analysis. The catalytic studies of hydrolysis and condensation carried out in NH_2/ZrO_2-doped microreactor and monofunctionalized microreactors indicated that the application of one-stage process translates to better overall performance. Polyamines as a base catalyst of the Knoevenagel reaction improve the efficiency and selectivity of the tandem process.

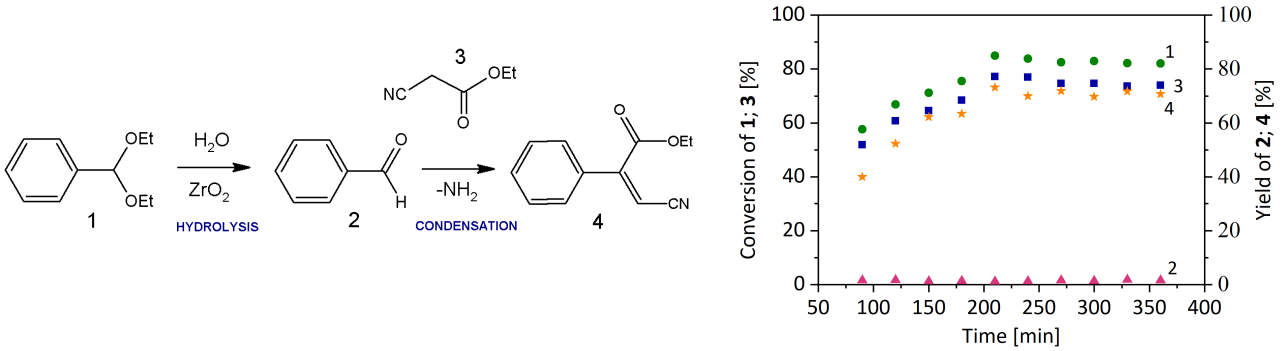

Figure 1. Scheme of domino process (left); conversion and yield vs. time for microreactor doped with zirconia and polyamine (right)

Acknowledgements.

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Simultaneous mesoporization and metal incorporation offers synthetic and catalytic benefits

Danny Verboekend*[1] and Martin d'Halluin[1]

[1]*Zeopore Technologies, Interleuvenlaan 23, 3001 Leuven, Belgium*
**danny.verboekend@zeopore.com*

Keywords: Mesoporous zeolite, metal deposition, bifunctional catalysis

Introduction. In many zeolite-based catalytic applications, a metal function is included to yield optimal performance. For example, in hydro-processing reactions, such as cracking and isomerization dewaxing, nickel is deposited on the catalyst to provide the required hydrogenation function.

Zeopore has achieved to combine high-quality mesopore formation with a controlled and highly tunable metal deposition (Figure 1). The method can be applied to any zeolite and most non-noble metals. Resulting metal-containing zeolites can then be shaped into catalysts, such as extrudates afterwards. Hence, the method of metal deposition is fundamentally different compared to standard metal-containing catalysts [1], in which first an extrudate is made, to be subsequently complemented with a metal using in an impregnation step.

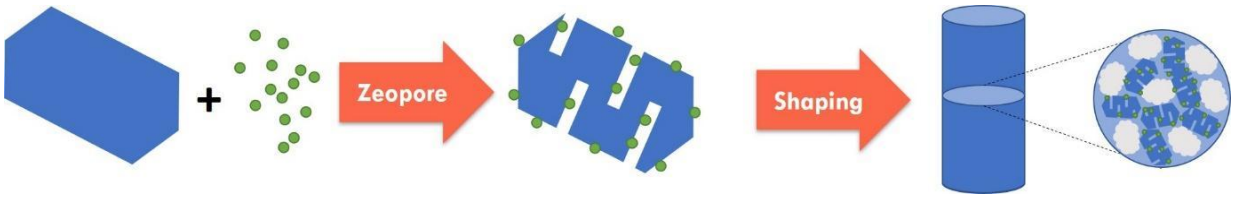

Figure 1: Zeopore's technology entails incorporation of metals (green) on the zeolite (blue) during mesoporization.

Experimental/methodology. The unique properties of Zeopore's metal-containing zeolites become obvious from almost any method of characterization. In the contribution, we will use various case studies, on for example Mg-ZSM-5, Mg-ZSM-23, and Ni-USY on both the powder and the extrudate level, to demonstrate how this class of materials contains superior porous properties, improved metal dispersions (near 100% dispersion), unique acidity profiles, and increased (hydro)thermal stability, using a variety of analytical techniques, such as N_2 sorption, FTIR spectroscopy with adsorbed pyridine, elemental analysis, chemisorption, and electron microscopy.

Results and discussion. Obviously, the proof of the pudding is in the catalytic performance. Zeopore is currently actively exploring the potential of this type of metal-containing zeolites in a number of applications, such as hydrocracking, dewaxing, methanol conversions, and aromatics conversion. We will demonstrate outstanding results in diesel dewaxing by hydro-isomerization using unidirectional zeolites, attaining -over standard mesoporous zeolites [2]- an order-of-magnitude lower diesel losses as a function of cloud point improvement and a simultaneous unique hydrogenation performance of aromatics present in the diesel feed. Also, a case on Mg-containing ZSM-5 in methanol to propylene will be demonstrated, evidencing, besides the expected 3-to-5-fold lifetime enhancement, an over 20% increased selectivity to propylene.

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Perovskites and exsolution treatment for catalytic purposes: the Methane Dry Reforming reaction

G. Da Pian[1], M. Pizzolato[1], E. Ghedini[1], A. Di Michele[2], F. Menegazzo[1], G. Cruciani[3], M. Signoretto[1]*.

[1]*Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, and INSTM RU of Venice Via Torino, 30172-Venice, Italy.*

[2] *Department of Physics and Geology, University of Perugia, Via Alessandro Pascoli, 06123-Perugia, Italy*

[3] *Department of Physics and Earth's Sciences, University of Ferrara, Via Giuseppe Saragat, 44123-Ferrara, Italy*

[*]*Corresponding Author's E-mail address: giulia.dapian@unive.it*

Introduction

Methane and carbon dioxide, the two most powerful greenhouse gases, can be exploit through Methane Dry Reforming reaction (MDR) to produce syngas in a more sustainable way. However, MDR is still not used at industrial level because of its high endothermicity, and easy deactivation of catalysts that are commonly supported ones. Deactivation occurs for two main reasons: carbon coke deposition and sinterization of active phase. To minimize these problems other classes of catalysts can be investigated. Perovskites should provide chemical and mechanical resistance, less coking, but also strong interactions of active phase with the bulk of material, and poisoning resistance [1]. This also thanks to a reducing treatment called "exsolution" [2], that is responsible of active phase formation. Exsolution should shape well anchored and dispersed nanoparticles on surface, formed by transition elements extracted from lattice. In this work, a base material was synthesized using lanthanum, iron and cerium, because of their coke resistance properties, and nickel, that is the active metal for MDR.

Materials and methods

The synthesis was carried out with the sol-gel method using nitrates salts as metal precursors, ethylen glycol and citric acid. The solid obtained was grounded and calcinated in air at 700°C for 4 h, divided into three parts and reduced under three different reducing conditions, at 800°C in H_2/He gasesous mixture. This to understand the effect of this treatment on activity and stability properties of the catalysts.

Results and discussion

The sample reduced with the lower heating rate (5°C/min) had the best MDR performance, with CH_4 and CO_2 conversions of 42% and 59% respectively in the first hours. TPR analyses showed different profiles for this catalyst, if compared with the other two that gave the same reduction peaks. This indicate the formation of different species on the surface of the best catalyst. SEM analyses further explained the different activity behaviours registered. On the surfaces of the reduced materials, particles were visible if compared with starting material that had a bare surface. The difference is on the best catalyst's surface, because better shaped and dispersed nanoparticles were formed, while on the other ones the surface seems to be damaged or bigger agglomerates were generated. By an XRD analyses it was possible to confirm the extraction of small cations from the lattice, so this could prove that exsolution happened. On spent catalysts was detected only amorphous carbon by TPO, an advantage for a future possible regeneration of this type of catalysts.

Conclusions

The three different exsolution conditions demonstrated how this treatment directly influences the catalysts activity and stability. This was confirmed from the analyses carried out on the catalysts, highliting the morphological and structural differences occurred thanks to exsolution. Further tests must be done to understand wich are the best conditions, but the results here reported show that this type of catalysts could be suitable for MDR purposes.

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Activity Enhancement in Au-Pd Bimetallic Systems as a Result of Co-Operation Between Individual Redox Reactions

Isaac T. Daniel[1*], Xiaoyang Huang[1], Ouardia Akdim[1], Mark Douthwaite[1], Kai Wang[1], Liang Zhao[1], Richard J. Lewis[1], Samuel Pattisson[1], Donald Bethell[1], Steven McIntosh[2] & Graham J. Hutchings[1]

[1] *Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, UK.*
[2] *Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA, USA.*
**Corresponding author: danielit@cardiff.ac.uk*

Introduction

Bimetallic Au-Pd catalysts are commonly seen to give significant rate enhancements over their monometallic analogues [1]. Herein, it is demonstrated that in catalytic alcohol oxidation over bimetallic Au and Pd catalysts, dehydrogenation (DH) and oxygen reduction (OR) can be coupled; a process termed Co-operative Redox Enhancement (CORE) [2]. Importantly, this mechanism enables significant DH rate enhancements to be achieved and is distinctively different to traditional synergy.

Experimental

Supported Au and Pd catalysts were synthesized by sol immobilization and the conversion of 5-hydroxymethylfurfural (HMF) was used as the model reaction. Both thermo- and electrocatalytic investigation were used to assess five catalytic systems. Amongst others, catalyst characterization was performed *via* scanning transmission electron microscopy (STEM) and x-ray photoelectron spectroscopy (XPS).

Results and Discussion

In the oxidative dehydrogenation (ODH) of HMF, a physical mixture of monometallic catalysts crucially shows a greater activity than a traditional alloy, with maximum activity observed for a supported Janus-type particle (Au@Pd/C) (**Figure 1a**). This highlights the importance of phase separation of active sites within the bimetallic system. Further thermochemical investigation shows that OR is intrinsically linked to the overall rate of ODH, and that the conductivity of the catalyst support is vital to facilitate electron transport. Therefore, a system is proposed whereby electrons produced during DH are consumed during OR, occurring over Au and Pd sites, respectively (**Figure 1b**). Electrochemical analysis, including linear sweep voltammetry, confirms the scheme and the specific roles of each metal. Finally, a kinetic model based on the CORE system accurately predicts the shape and maxima of activity across a range Au/Pd molar ratios (**Figure 1c**) [3]. This CORE effect is a wholly new observation which could change how researchers approach catalyst and process design.

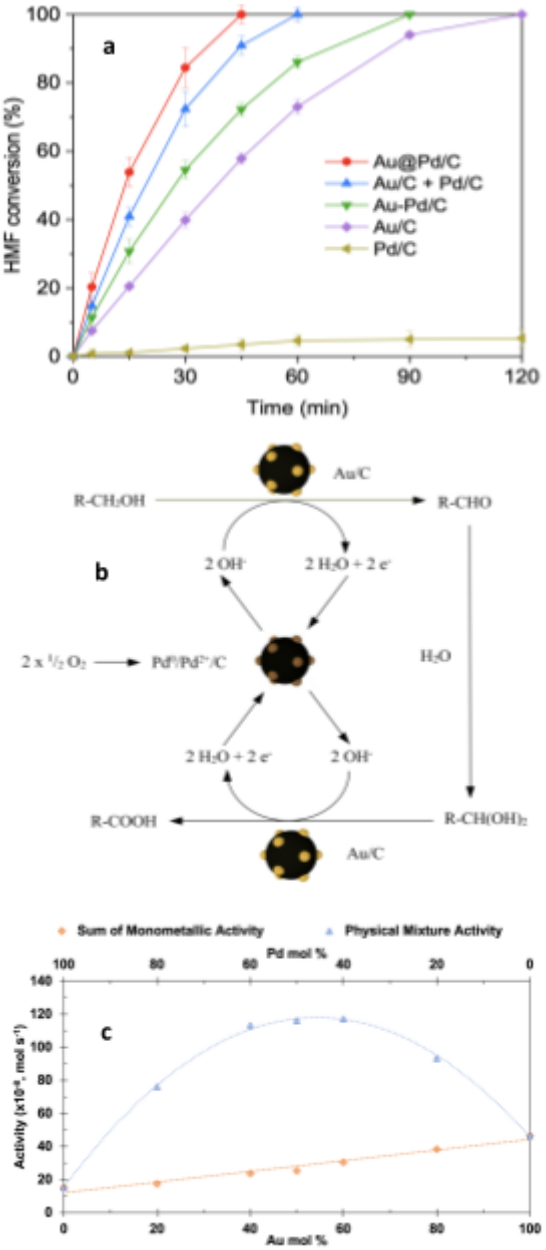

Figure 1. (**a**) HMF ODH over two hours for five different catalytic systems. (**b**) The proposed CORE system for supported Au and Pd catalysts. (**c**) The activity enhancement due to CORE effects over a range of molar ratios for a physical mixture catalytic system.

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Metal-Organic Framework-derived Catalysts for Upgrading of an Acetone-Butanol-Ethanol (ABE) mixture

K. Deekamwong[1,2*], C. Phawa[1], J. Wittayakun[1], S. Prayoonpokarach[1]

[1]*School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, Thailand*
[2]*Institute of Research and Development, Suranaree University of Technology, Nakhon Ratchasima, Thailand*
[*]*Krittanun.d.aa@g.sut.ac.th*

Keywords: MOFs, Acetone-Butanol-Ethanol

Introduction : An intermediate mixure of acetone, butanol, and ethanol (ABE) produed by fermentation from biomass have been currently gaining significant attention for making high-value chemicals and fuels [1]. This ABE udgrading required a metal/metal oxide catalysts with a high reaction temperature (160-300 °C) under autogeneous pressure to create the coupling alcohol/ketone products. There are some reports revealed that the use of magnesium or aluminium oxide-based catalysts can transform the ABE mixture. Those catalytic performance exhibited good activities. However, a modification of such catalyst type is difficult to enhance selectivity and productivity [2]. Therefore, the development of catalyst capable of efficient and selective transformation of ABE is still a formidable challenge. Herein, we aimed to explore the heterogeneous catalytic ABE updgrading reaction by using metal-organic framework-derived catalyst which is easier to design and functionallization. Moreover, the correlation between the upgrading products and physicochemical properties and reaction parameters will be investigated.

Experimental/methodology : In a typical reaction condition, 10 mg of Ni-ZIF-8 and 0.5 mL ABE mixture with/without K_2CO_3 were added into a 0.6-mL micro-reactor maded by stainless steel tube reactor, capped, and then heated to a desired temperature for 24 h. After cooling down, the product mixtures were analyzed by GC-FID and GC-MS. The spent catalysts were further charaterized by several X-Ray techniques, spectroscopic techniques.

Results and discussion : The ABE conversions demonstrated a modest catalytic activity in the absence of a catalyst, as indicated in Table 1. While employing Ni-ZIF-8, the conversions were increased by more than double. Similar compounds produced under both conditions include aliphatic ketones like 1-butanal and 3-heptene-2-one. In contrast, the reduction in overall ABE conversions was seen when Ni-ZIF-8 and K_2CO_3 were used as catalyst and co-catalyst, respectively. However, alicyclic ketone such as isophorone and 3, 5-dimethyl-2-cyclohexene-1-one were mainly produced. The product selectivity may result from acid-base properties of the catalysts. These results suggested the use of ZIF-derived catalyst are promising heterogeneous catalyst for ABE upgrading.

Table 1. Catalytic performance of ABE upgrading reaction

	Catalyst		
	none	**Ni-ZIF-8**	**Ni-ZIF-8 with K_2CO_3**
Acetone conversion	38.7	63.8	75.1
Ethanol conversion	25.2	38.9	43.4
***n*-butanol conversion**	22.3	30.9	35.7
Major product	Aliphatic ketone (C5-C7)		Alicyclic ketone (>C8)

Acknowledgments

This work was supported by (i) Suranaree University of Technology (SUT) , (ii) Thailand Science Research and Innovation (TSRI) , and (iii) National Science, Research and Innovation Fund (NSRF) (179259)"

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The transesterification process of vegetable oils based on heterogeneous catalysts of rare and alkaline earth metals

D. Dendek[1*], M. Zakrzewski[1], T. Maniecki[1]

[1]*Department of Chemistry, Institute of General and Ecological Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland*

[*]*daria.dendek@dokt.p.lodz.pl*

Keywords: biodiesel; transestrification; vegetable oils, heterogeneous catalyst

Introduction. One economically produced method of biodiesel is the transesterification of vegetable oils. Currently, different types of catalysts such as homogeneous and heterogeneous are used. However, the latter shows greater efficiency, multiple use, and environmental friendliness. Alkaline and rare earth metals in particular are recoverable and can give high-quality products. For example, calcium oxide (CaO) is a commonly used component of catalytic systems in the production of biodiesel in the transesterification process due to its wide availability, low cost, and non-corrosive. Another example is La_2O_3, which provides stability and prevents the washing out of the active ingredient during the transesterification reaction. Yan et al. in their work found that the system containing La_2O_3 and CaO is resistant to oil feedstocks containing a high content of free fatty acids in the transesterification process [1]. The addition of lanthanum may affect the stability of the system and the possibility of obtaining higher activities. The aim of the work is to optimize the transesterification process based on systems based on La_2O_3 and CaO and to find a correlation between the alkalinity/acidity of the surface and the activity of the catalyst.

Experimental/methodology. The CaO-Al_2O_3, La_2O_3-Al_2O_3, and La_2O_3-CaO catalysts were prepared in two stages. First of all, Al_2O_3 and CaO supports were obtained by the precipitation method using ammonia water or sodium hydroxide as precipitation agents. Then, the Al_2O_3 compound was covered with CaO in the ratio of 70:30 and 50:50, and La_2O_3 in the ratio of 70:30 using wet impregnation. The La_2O_3-CaO system (ratio 30:70) was synthesized also by impregnating CaO using lanthanum (III) nitrate (V) salts. Finally, the catalysts were calcined at 800 ℃ for 4 hours. The obtained catalytic systems were subjected to physicochemical tests: X-ray diffraction (XRD), Atomic Absorption Spectrometry (AAS), and Temperature programmed desorption (TPD-CO_2). The catalytic systems were subjected to the transesterification process in various conditions (p = 1atm, temperature range 50 – 150 °C, time = 0.5 – 1.5h) using an autoclave and then the resulting solution was tested using high-performance liquid chromatography (HPLC).

Results and discussion. The prepared catalytic systems were subjected to the transesterification process, in which 30 ml of rapeseed oil, 10 ml of methanol, and 250 mg of catalyst were used each time. After the process, the product was separated from the catalyst and subjected to HPLC tests, which allowed us to calculate the conversion of triglycerides. The obtained conversions of the 5 main components of rapeseed oil were very similar, therefore they were averaged and presented in

Table 1. XRD studies of the above catalytic systems showed the presence of CaO, La_2O_3, and Al_2O_3 structures depending on the used sample. The AAS study allowed us to confirm that the content of calcium and lanthanum in the catalytic systems agrees with the amount initially introduced into the systems. TPD-CO_2 studies showed that the CaO-based system has more basic sites than the La_2O_3 system, which is in good agreement with the conversion results.

Table 1. Triglyceride conversion for the used catalytic systems.

Catalyst	Conversion [%]
La_2O_3/Al_2O_3 70:30	28
CaO/Al_2O_3 50:50	28
CaO/Al_2O_3 70:30	36
La_2O_3/CaO 30:70	96

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Fly ashes from energy sector as attractive precursors for synthesis of catalytic materials

P. Rybowicz[1], R. Panek[2], A. Łagosz[3], B. Gil[1], W. Roth[1], W. Franus[2], A. Adamski[1*]

[1]*Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, PL 30-387 Krakow*
[2]*Lublin University of Technology, Faculty of Civil Engineering and Architecture, Nadbystrzycka 40, PL 20-618 Lublin*
[3]*AGH-University of Science and Technology, Faculty of Material Science and Ceramics, Mickiewicza Ave. 30, PL 30-059 Krakow*
[*]*a.adamski@uj.edu.pl*

Introduction. Fly ashes are generated worldwide on a massive scale because of industrial energy production from fossil fuels based on coal and heavy oil combustion. Through the last few decades, there was a lot of studies focused on various methods of valorization of fly ashes (FAs). However, one of the most ambitious applications is the use of FAs as precursors to obtain functional materials such as catalysts, catalytic supports, or sorbents. In this work we discuss several representative examples of efficient use of FAs as valuable precursors to synthesize i) advanced materials of catalytic importance, including oxide phases active in such reactions as DMR, deNO_x, deSoot or ammonia oxidation, ii) supports for transition metals or metal ions tailored for catalytic systems applied e.g., in CO_2 hydrogenation or iii) in synthesis of zeolites. Our goal was to select and to indicate the decisive parameters of fly ashes, determining their possible catalytic applications [1]. Such sustainable pro-ecological approach remains in agreement with principles of circular economy and permits to exploit high potential of fly ashes as synthetic raw materials.

Experimental/methodology. Six types of FAs obtained from industrial coal-fired power plants have been investigated to be used as starting components for synthesis of catalytic materials mentioned above. All ashes were generated by coal combustion in pulverized-fuel boilers. Additionally, one type of ash generated during heavy oil combustion has also been studied. Bare oxides, supported oxide systems containing both support and active phase prepared from fly ashes as well as NaX and MCM-22 zeolites were synthesized by optimized wet chemistry procedures. All FAs used for syntheses and the obtained new materials have been
in-depth characterized by XRF, XRD, RS, BET, SEM and DRIFT.

Results and discussion. The results of structural, textural and functional characterization of FAs as starting components for synthesis of both oxide systems and zeolites have been obtained [2]. Optimized parameters and dedicated synthetic pathways ensuring high efficiency towards target products and giving a possibility to control surface architecture of the final systems, have been proposed. The role of such critical parameters as the presence of residual carbonaceous impurities, the content ratios of the glass to crystalline phases or Si to Al have been elucidated. Moreover,
the importance of such textural properties as specific surface areas, particle types and their size distributions have been analyzed in detail. The obtained results clearly confirmed the complex nature of the fly ashes and their evident potential to be used for synthesis of such functional materials as e.g., oxide catalytic systems or zeolites.

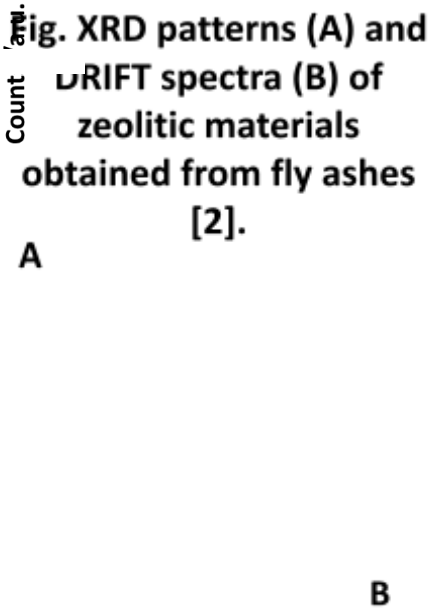

Fig. XRD patterns (A) and DRIFT spectra (B) of zeolitic materials obtained from fly ashes [2].

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Aluminium and Acid Site Evolution during Zeolite Crystallization and Thermal Activation

J. Devos[1*], S. Robijns[1], I. Khalil[1], M. Dusselier[1]

[1]*Center for Sustainable Catalysis and Engineering (CSCE), KULeuven, 3001 Leuven, Belgium*
[*]*julien.devos@kuleuven.be*

Keywords: zeolites; synthesis; crystallization, ozone, acid site distribution

Introduction. Despite extensive tuning of zeolite catalyst, little is known on the synthetic origin of acid sites and their distribution at the sub-nanoscale. Even more, the effect of calcination is often unconsidered. This work demonstrates bottom-up rational selection criteria for synthesis of SSZ-13 (CHA) and ZSM-5 (MFI) with tuned Al and acid site distributions. It is demonstrated that Al and acid siting change during prolonged synthesis and during thermal activation. Many recent findings suggest that zeolite catalysis is influenced by synergistic effects (BAS-BAS; BAS-LAS) derived from acid site proximity or Al distribution.[1] Next to adequate post-synthetic treatments,[2] delicate engineering of zeolite crystallization (synthesis) is possible with control over crystal dimensions, morphology and charge deficit. Hence, synthesis is an important consideration when making application oriented materials with tuned Al and acid site proximity.
Experimental/methodology. Five crystallization systems are studied yielding ZSM-5 (MFI) and SSZ-13 (CHA), made either via interzeolite conversion or conventionally.[3,4] Synthesis evolution is tracked in time for stoichiometrically identical synthesis systems, obliviate the used SDA ($1Si:0.025Al:0.35SDA^{+}:0.35OH:{\sim}15H_2O$). The synthesis output is analysed via elemental analysis, P-XRD, N2-physisorption, (D)TGA, TEM-EDX and (Pyridine) FT-IR and aqueous Co^{II}-exchange (DCC).
Results and discussion. Overall, Al was identified as key component during all stages: (FAU) dissolution, nucleation, assembly and maturation. The latter is generalized through an in-depth comparison with literature.[5] Single-parameter variations applied during synthesis of siliceous SSZ-13 showed that both kinetic and thermodynamic components influenced Al distribution.[3] Most significantly, it was found that internal arrangement of Al in SSZ-13 still evolves with synthesis time. The extent of synthesis evolution varies dependent on the synthesis system (OSDA-zeolite combo), which was previously unreported in literature. TPA/Na containing ZSM-5 has a strongly evolving DCC, whilst no DCC evolution is detected over (oven) time for TMAda/Na containing SSZ-13.[4] Our work adds novel insights on the synthesis processes that regulate the final acid site distributions within zeolites by taking into account the mobility of ionic charge. It is proposed that internal rearrangement of Al occurs at the level of cages towards more thermodynamically favored Al (charge) separation.[4;6] Furthermore, Al distributions are also found to change with calcination. We engineered a low-temperature ozone activation process for zeolites.[7] In parallel to Al mobility upon prolonged synthesis, elevated calcination temperature also affects the internal Al distributions, as well as Al speciation. A picture is drawn how Al speciation evolves with activation temperature, also taking into account the synthesis-specific reality (crystal size, stability, etc.).[8] Understanding the mostly unconsidered effect of 'synthesis + activation temperature' may not only help to explain conflicting literature reports, but it may also significantly enlarge the toolbox for bottom-up rational engineering of future catalysts.

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Mechanistic Insights into the Solid-State Crystallization of High-Density Zeolite

D. Dey[1] and M. Kumar[2*]
[1]*Indian Institute of Technology, Department of Chemical Engineering*
Hauz Khas, New Delhi (India), 110016
[2] *Indian Institute of Technology, Department of Chemical Engineering*
Hauz Khas, New Delhi (India), 110016
[*]*manjeshkumar@chemical.iitd.ac.in*

Introduction. Zeolite with its unique pore architecture and tunable acid site distribution has emerged as a prominent candidate in the multi-dimensional application field[1]. Conventional synthesis of zeolite in the solvothermal process includes several disadvantages including high solvent consumption, low yield, high operational pressure, and environmental concerns making these processes economically challenging. To mitigate these challenges, researchers have developed various new strategies. Recently, a new pathway, the solid-state transformation has been reported which has the potential to become the greener approach to synthesizing zeolite for the industry with commercial profitability. Although studies have successfully postulated the formation mechanism of several zeolite frameworks, the control over morphological growth and hence the intrinsic properties is still elusive[2]. Our work has established mechanistic insights into the crystallization of zeolite in solid-state synthesis.

Experimental/methodology. The pure cancrinite phase was synthesized by taking the solid raw materials in appropriate quantities into a mortar pestle, grinding the solid mixture for at least 20 minutes, and then transferring it to the Teflon-lined acid bomb digestor. After that, it was heat treated various times at 120˚C. The solid product was washed thrice with DI water while centrifugation, after which dried at 60˚C overnight and collected.

Results and discussion. In this study, we have investigated the mechanistic insights of a zeolite framework, CAN synthesize via solid-state transformation. Systematic powder X-ray diffraction studies of the samples synthesized after 24, 36, 48 and 72 hrs. have revealed the presence of an initial slow crystallization process up to 36 hrs. followed by an accelerated growth phase producing a complete crystal phase after 48hrs. suggesting the presence of typical complex reactions at the initial stage that occurs in the hydrothermal synthesis of zeolite[3]. Morphological evolution study using scanning electron microscopic (SEM) images revealed to form a unique 'dendrimeric' shaped morphology whose surfaces were seemed to highly roughen as they comprised domains of spheroidal particles. These rough surface starts to smoothen with further heating up to 72 hrs (figure 1E). The investigation of the nanoparticle agglomeration phenomenon using HRTEM imaging revealed the attachment of nanoparticles among themselves and with the bulk through typical crystallographic planes of the CAN phase. Domains having nanoparticles with oriented attachment can be seen in images H and I. Although, the common crystal plane varies with the different positions of the particle. This suggests the formation of individual domains having the single-crystal-like feature. These domains finally agglomerate to form the final bulk particle which is a meso crystal rather than a single crystal as complete grain boundary migration is still elusive. Based on these observations it can be suggested that in solid-state transformation, nanoparticles tend to follow a hybrid non-classical mechanism for morphological growth.

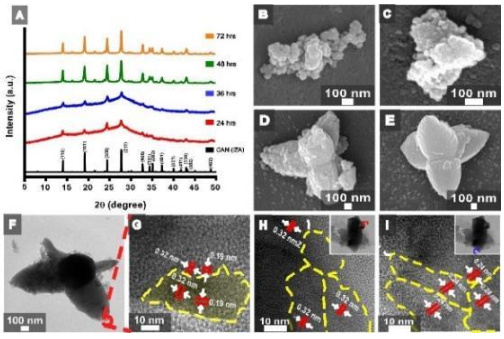

Figure 1. The figure illustrates powder XRD pattern of the synthesized solids depicted in the image (A), the (B-E) (SEM) images of the as-synthesized particles. (F-I) HRTEM image was taken for the particles synthesized after 72 hrs. of heating.

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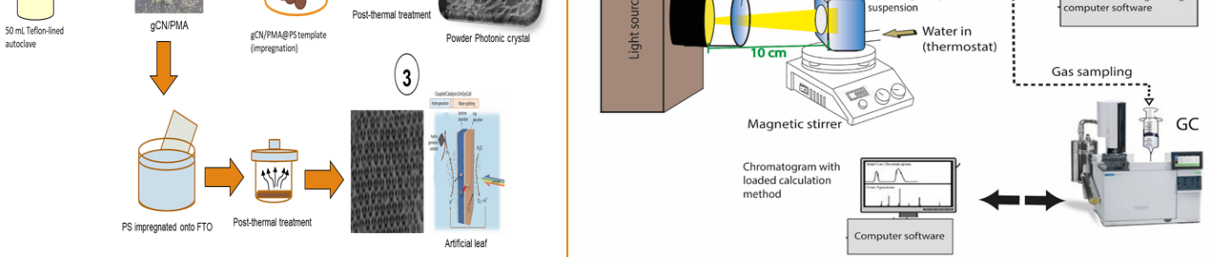


Doped g-C_3N_4 based photonic crystals enhancing light-driven of catalyzed reactions

Simon Y. Djoko[1], Micahel Schwarze[1], Prasenjit Das[2], Julia Grüneberg[2], Vincent Weigelt[2], Edith Mawunya Kutorglo[1], Dung Nguyen D.[1], Arne Thomas[2], Reinhard Schomäcker[1*]

[1]*Technische Universität Berlin, Reaction Engineering Group, Berlin, Germany*
[2]*Technissche Universität Berlin, Functional Materials, Berlin, Germany*
[*]*schomaecker@tu-berlin.de*

Keywords: Doped g-C_3N_4, Photonic crystals, light-driven reactions, H_2O_2 synthesis, PEC water splitting

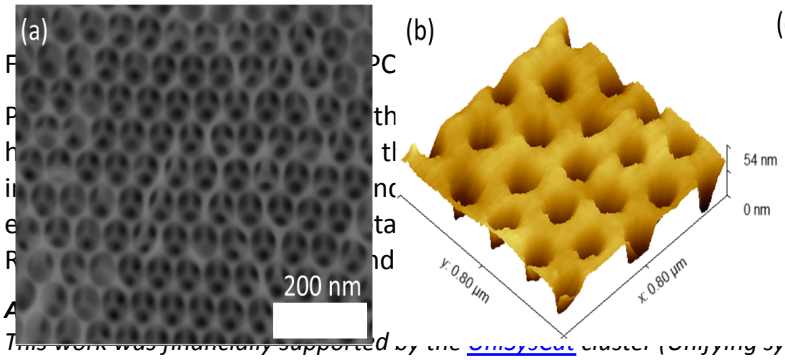
Introduction.
When used as a photocatalyst for light-driven catalyzed reactions, graphitic carbon nitride[1] (gCN) exhibited very low catalytic performances due to the slow charges separation and their fast recombination but, at least it provides one of the best chemical frameworks for the synthesis of highly efficient photocatalysts useful to better achieve the light-harvesting process[2,3]. In this study, we fabricated for the first time a photonic crystal material like inverse opal structure made up P-doped gCN backbone with metal ions confined in the lattice structure then, the PC has been applied as photocatalyst for efficient light harvesting and charge separation in photocatalytic H_2O_2 synthesis, hydrogen evolution and photo-electrochemical water splitting.

Experimental/methodology.

Figure 1: Synthesis method of PCs (a), Experiemntal photocatalytic setup for catalyzed reactions (b).

As displayed in figure 1.a, the synthesis method consisted first of the preparation of a bulk composite made up gCN and polyoxometalate (POM). By a chemical wet impregnation, a colloidal solution is then formed by immersion of the bulk solution into a dispersion of Polystyrene spheres. After post-thermal annealing, the final P-doped PC was obtained and characterized. By the use of the experimental setup, as displayed in figure 1.b, the PCs samples were applied for light-driven H_2O_2 synthesis and hydrogen evolution. PEC was also used for overall water-splitting reactions.

Results and discussion.



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This work was financially supported by the Unity cluster (Unifying System in catalysis) and the Einstein Centre of Catalysis (EC2) of the Technische Universität Berlin. Simon Yves Djoko is grateful to the Berlin International Graduate School of Natural Sciences and Engineering (BIG-NSE) for the doctoral training program. He gratefully acknowledges the big contribution of the Elsa Neuman Stiftung of the Berlin state for the scholarship provided.

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Facile synthesis of Au/SiO_2 nanostructures: from 1D to 3D nanotube networks using polycarbonate membranes as template

F. Drault[1,2], S. Hermans[1], S. Demoustier-Champagne[2]

[1] IMCN (MOST division), UCLouvain, 1 Place Louis Pasteur, B-1348 Louvain-la-Neuve, Belgium.
[2] IMCN (BSMA division), UCLouvain, Croix du Sud 1, B-1348, Louvain-la-Neuve, Belgium
contact e-mail: fabien.drault@uclouvain.be

Introduction. Tuning silica (SiO_2) nanostructures from one-dimensional (1D) to three-dimensional (3D) nanotubes (NTs) networks is of great interest. Indeed, free-standing 3D SiO_2 NTs membranes could be useful for several applications, and in particular for heterogeneous catalytic systems involving flow chemistry and continuous processes[1]. Indeed, SiO_2 is a well-known catalysis support with a high versatility for tailoring. The advantage of the proposed nanotubes synthesis method resides in the possible multi-functionalization of their inner and/or outer surfaces by different active sites, which could be incompatible when in direct contact. To this aim, polycarbonate track-etched (PCTE) membranes (provided by it4ip) with an interconnected cylindrical nanopores system have been used as template[2].

Experimental/methodology. The synthesis of 3D SiO_2 NTs (Figure 1) consists in the two following steps: sol-gel deposition[3] within the pores of the PCTE membranes and extraction of this template. In addition, selective gold nanoparticles (Au NPs) functionalization of the SiO_2 nanotube's inner surface has been performed by electroless deposition[4].

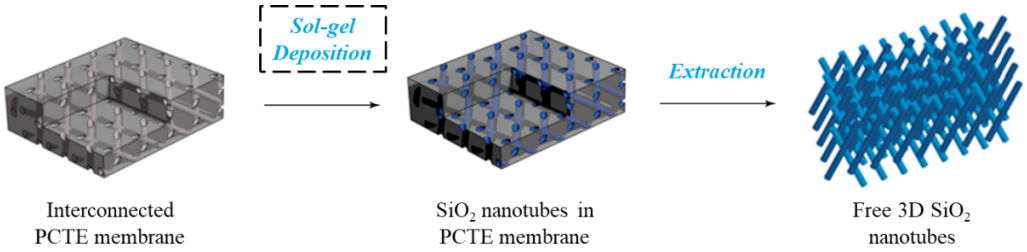

Figure 1 – Two step synthesis for the production of free 3D SiO_2 NTs using interconnected PTCE membrane.

Results and discussion. The obtained nanostructures were characterized by multiple techniques (i.e. electron microscopy (Figure 2), XRD, N_2 physisorption, XPS) at each step of their elaboration, allowing the identification of key parameters to control silica sol-gel and gold electroless deposition. Interestingly, 1D and 3D SiO_2 NTs with different structural porosities were succesfully prepared and, the NTs porosity was shown to strongly impact the subsequent Au deposition process. Indeed, different Au amounts were deposited, ranging from 11 to 4 wt.% at the surface of mesoporous and non-porous SiO_2 NTs, respectively, indicating that Au NPs are mainly localized inside the SiO_2 tubes when their pore walls are non-porous.

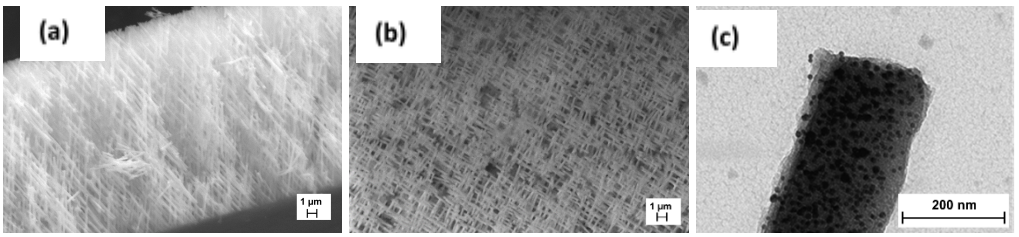

Figure 2 – SEM images (a) of the side, (b) top view of the obtained free-standing 3D SiO_2 NTs functionalized by Au NPs and (c) TEM image of a single SiO_2 NTs functionalized by Au NPs.

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The reduction/oxidation potential of nickel, cobalt, and copper oxides derived from various precursors

P. Gwóźdź, A. Łącz, S. Komarek, K. Kornaus, E. Drożdż*

AGH University of Science and Technology in Krakow, Faculty of Materials Science and Ceramics, Poland
**edrozdz@agh.edu.pl*

Keywords: nickel oxide, cobalt oxides, copper oxides, nitrate precursor, acetate precursor, catalyst

Introduction. Ni, Co, and Cu oxides are one of the most commonly used materials in environmental catalysis and/or for energy conversion technologies. However, the catalytic abilities of these oxides are strongly related to their physiochemical properties such as particle size and particle size distribution, specific surface area (SSA), and the oxidation state of metal in the oxides' structure. The motivation to start the presented research was the diverse and often inconsistent results of temperature-programmed reduction studies conducted on the above-mentioned oxides presented in the literature.

Experimental/methodology. Ni, Co, and Cu oxides were obtained by the thermal decomposition of proper acetates and nitrates. The various heating rates were applied – 1 deg/min and 10 deg/min to achieve a different morphology. The obtained powders were characterized in terms of phase and chemical composition (XRD, EDS), microstructure (SEM, BET, DLS – *Dynamic Light Scattering*), and reduction properties (TPR/TPOx). Additionally, commercially available Ni, Co, and Cu oxides were characterized and used as reference materials.

Results and discussion. The results of phase composition analysis showed that regardless of the precursor used (nitrates or acetates) the final products of the decomposition are the proper oxides - NiO, Co_3O_4, and CuO. TG/DTA curves for the thermal decomposition of nickel, cobalt, and copper nitrates are shown in Figure 1. The obtained oxides, derived from various precursors, do not differ significantly in the specific surface area and particle size distribution within the applied heating rate. However, these parameters are different when comparing the oxides obtained with different heating rates. To determine the influence of the microstructure of the powders on their reducing properties mainly, the temperature of reduction beginning, and the character of the TPR profiles (the number of reduction peaks and maximum temperature of the reduction peaks) TPR measurements were carried out for materials obtained by the thermal decomposition of both precursors. In addition, TPR measurements of reference materials were carried out. These oxides were also characterized in terms of their structure and microstructure.

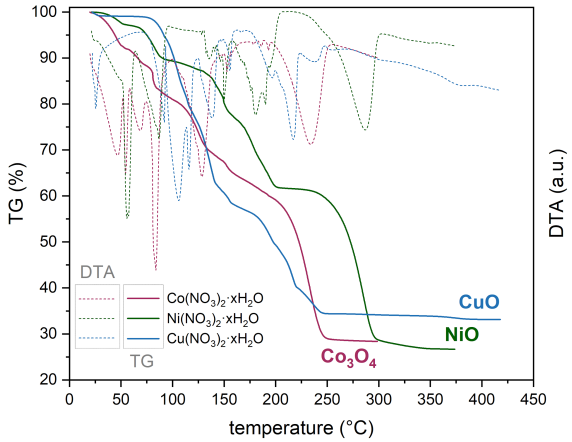

Figure 1. The TG/DTA curves of thermal decomposition of Co, Ni, and Cu hydrate nitrates.

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P, O-co-doped carbons as a catalysts in 1-cloro-4-nitrobenzene hydrogenation

E. S. Duran-Uribe[1*], E. V. Ramos-Fernadez, A. Sepulveda-Escribano

Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica – Instituto Universitario de Materiales de Alicante, Universidad de Alicante, Alicante, Spain

Keywords: Doped carbon, nitroarenes reduction, metal-free catalyst

Introduction. The catalytic hydrogenation of nitroarenes to obtain anilines has received great industrial interest, due to the simplicity of the process and the low by-products formation [1]. Doped carbon-based materials are promising candidates for their use as metal-free catalysts in chemical reduction of nitro compounds [2]. Some studies have shown that surface modification of carbon with heteroatoms such as N improves the catalytic activity [3]. However, a study on the effect of oxygenated groups on activated carbons, as well as the effect of different types of phosphorus, has not been carried out. Therefore, in this study the use of O- and P-doped carbons for the hydrogenation of 1-chloro-4-nitrobenzene was proposed. In addition, the effect of the different functional groups and synthesis methods on the catalytic activity was studied.

Experimental For the preparation of O-doped carbons, RGC30 (commercial mesoporous carbon) was stirred for 48 h in a 6 M H_2O_2 solution and then washed with water several times. Finally, the generated oxygen surface groups were partially removed by heat treatment in an inert atmosphere. For the preparation of P, O-codoped carbon the RGC30 and PA (phytic acid) were mixed and subsequently pyrolyzed in a furnace under inert atmosphere at different temperatures. The catalysts were finally tested in the hydrogenation of 1-chloro-4-nitrobenzene (CNB) using hydrazine as reducing agent.

Results and discussion After pyrolysis of PA and RGC30, the presence of phosphorus in the carbon was observed by XPS, which is characterized by peaks from 132 to 134 eV in the P 2p region in all catalysts. Furthermore, it was observed that different phosphorus functional groups were obtained depending on the pyrolysis temperature, the amount of PA and the pretreatment of the precursors. The synthesis route in which PA is polymerized on RGC30 was found to be the most suitable one, resulting in surface phosphorus with a binding energy close to that of C_3PO, where phosphorous is inside the carbon structure (132 eV). On the other hand, the synthesis route in which there was no pretreatment prior to pyrolysis is the most suitable one for obtaining phosphorus outside the carbonaceous structure, as CPO_3 (133,5 eV). Finally, an increase in the oxygenated groups was observed after treatment with H_2O_2. An increase in quinone, ester, anhydride and carboxyl groups was observed. However, when the catalyst was treated at 900 °C in an inert atmosphere, a decrease in quinone and carboxyl groups was observed. When testing the catalytic activity for the hydrogenation of CNB (**Fig. 1**), it was observed that, regardless of the treatment of the catalyst, a selectivity of more than 99% is obtained for chloroaniline. The treatment significantly affects the activity. The oxidised catalyst (RGC30_OX) shows better catalytic activity than RGC30. In addition, an increase in catalytic activity was observed when the catalysts was doped with P (RPA1.0P9PP, RPA1.0P9PP_OX).

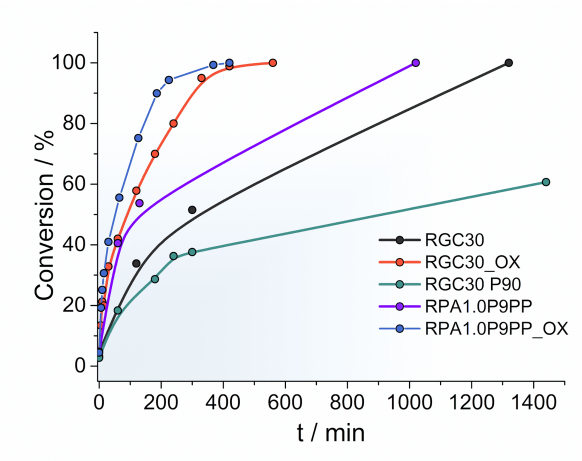

Figure 1. Results of catalytic tests in the reduction of 1-chloro-4-nitrobenzene with P,O- codoped catalysts

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Phosphorus-modification of Pt-catalysts boosts the catalytic performance in cycloalkane dehydrogenation

A. Ellert[1], F. Herold[2], A. Hutzler[3], T. Janssens[4], P. Vennestrøm[4], P. Wasserscheid[1], P. Schühle[1*]

[1]*Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen, Germany*
[2]*Norwegian University of Science and Technology (NTNU), Trondheim, Norway*
[3]*Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), Erlangen, Germany*
[4]*Umicore Denmark ApS, Hørsholm, Denmark*
[*]*patrick.schuehle@fau.de*

Introduction. By tuning the concentration and location of catalyst dopants, such as sulfur or phosphorus, the properties of catalysts can be changed. A known example is the doping of Pt-catalysts with sulfur in the dehydrogenation of hydrocarbons. The sulfur-dopant blocks strong adsorbing Pt-sites, which leads to a simultaneous increase in activity and selectivity.[1] Phosphorus can also influence the properties of the catalytically active metal by changing the electronic and geometric properties of the metal particles in the catalyst.[2,3] In this study, we show a promising effect of P-doping for Pt-catalysts, distinctly increasing their catalytic activity in cycloalkane dehydrogenation.

Experimental/methodology. Two different P-modification methods are developed and compared. The first method involves wet impregnation of a Pt/Al_2O_3 catalyst with phosphorous acid, followed by a reduction with hydrogen. The second method involves the decomposition of sodium hypophosphite at temperatures above 250 °C in a furnace upstream of a Pt/Al_2O_3-catalyst, by which a P-doped Pt-catalyst is obtained.

Results and discussion. It is observed, that reduction temperatures of 600 °C are required to fully activate a P-doped Pt-catalyst for the dehydrogenation of perhydrobenzyltoluene (H12-BT), to obtain a higher activity than the corresponding P-free material. At the same time, the pure Pt/Al_2O_3 suffers from sintering at high reduction temperatures, an effect that is efficiently suppressed by P-doping (Figure 1).

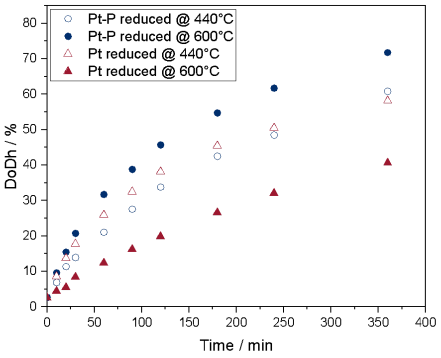

Figure 1 Degree of dehydrogenation (DoDh) over time for 3 wt.% Pt-catalysts with and without 0.9 wt.% P, supported on Al_2O_3, reduced at 440 or 600 °C. Catalysts tested at H12-BT:Pt = 2000:1. 15 g H12-BT, initial inertization with Ar, reaction at 250 °C, 1 atm. Degree of dehydrogenation measured *via* refractive index.

In addition, setting an optimal P:Pt-ratio is essential to achieve high activities, since both, too low and too high levels of phosphorus lead to an activity loss. Investigations using TEM revealed that the Pt-P-catalysts have average particle sizes below 1 nm despite the high-temperature reduction step. To understand the effect of P-addition *via* the two synthesis methods, XPS, STEM-EDX, CO pulse chemisorption and NH_3-TPD measurements are conducted. With these studies material properties, such as particle sizes and distribution, electron density, as well as surface acidity are elucidated. In summary, the here presented study gives insights into the function and role of phosphorus in P-modified transition metal catalysts and demonstrates the high potential of these materials for dehydrogenation reactions and their high-temperature stability.

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Fluorination of novel Cu/ZnO/MgO Methanol Catalysts to improve Productivity and Selectivity

Lukas D. Ernst[1,2], Sebastian Polinski[1,2], Ingo Krossing[1,2*]

[1] *Freiburg Materials Research Center, University of Freiburg*
[2] *Insitute for Analytical and Inorganic Chemistry, University of Freiburg*
[*] *krossing@uni-freiburg.de*

Keywords: Methanol Synthesis, CO_2 hydrogenation, heterogenous catalysis, fluorination

Introduction. The largest part of todays produced methanol is synthesized based on fossil resources *via* a catalytical process. Regarding the current climate problem, a more sustainable synthesis route such as the hydrogenation of CO_2 would be desirable. In almost all industrial MeOH catalyst systems, the actual catalysis is mainly based on the catalytically active Cu/ZnO pair, with one or more supporting oxides (such as Al_2O_3, called support or promotor[1]) being added. For a MeOH synthesis from CO_2 and H_2 instead of CO and H_2, Al_2O_3 is unsuitable as a promotor, here ZrO_2 was discovered as a promising alternative (CZZ system).[2] Investigations on binary Cu/ZnO systems have shown that treatment with fluorine increases MeOH productivity and selectivity.[3,4] When trying to transfer the positive effect of fluorination to the ternary CZZ system, it was found that Zr acts as a "fluorine magnet" and no positive effect on productivity or selectivity is observed.[5] This work deals with Mg as an alternative to Zr that is compatible with the fluorination process.

Experimental/methodology. Catalyst materials were prepared *via* a conventional co-precipitation method: nitrate salts of the metals (Cu, Zn, Mg) were dissolved in H_2O and precipitated by adding Na_2CO_3 solution (1 M) while temperature and pH were kept constant. The precipitated products were then washed and dried in a spray drying process. Afterwards, these precursors were calcinated (300 °C) and a further treatment was done by reaction of the precatalysts with F_2. Catalysis testing was done at 250 °C and 40 bar, $CO_2 : H_2 = 1 : 3$. The outlet gas stream was analyzed by an in-line gas chromatograph. Further characterization techniques for the catalyst materials were ICP-OES, SEM, EDX, pXRD, IR-spectroscopy, fluoride ion chromatography, XPS, N_2-physisorption (BET) and TGA.

Results and discussion. Several different catalysts with different compositions (Cu : Zn : Mg = 3.75 : 1.73 : *X*; *X* = 0.5, 1.0, 2.0) and under different synthesis conditions (variation of synthesis temperature, pH and aging time) were produced. A total of 5 different CZMg systems were produced, all of which were treated with about 1.4 wt% F_2, thus 10 different systems were obtained. The catalyst systems show good tunability in their physical and chemical properties as well as in their catalytic properties. The treatment with fluorine (1.4 wt%) leads in all cases to an increase in the methanol productivity (see figure 1, up to 150 %) and selectivity. In the case of MeOH productivity, this is most likely due to an increase in the number of ZnO_{1-x} defect sites.[3,4] The increase in the MeOH selectivity is most likely due to an increase in the activation energy for the competing RWGS reaction.[4] Interestingly, an increase in fluorine content leads to a significantly increased long-term stability, which is the subject of our current research.

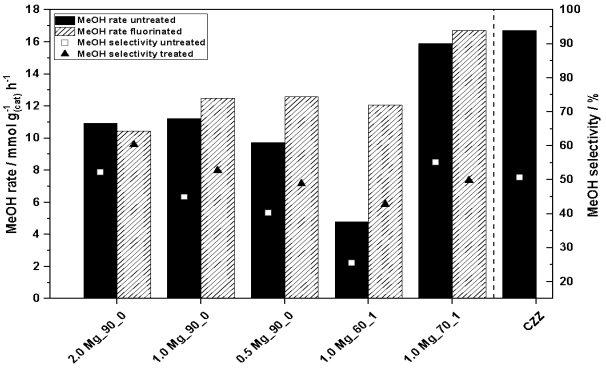

Figure SEQ Figure * ARABIC 1. MeOH rates and selectivities of all synthesized catalyst systems (in pairs untreated and fluorinated). The data set of the CZZ benchmark system has been added for comparison.

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Biodegradable polymer synthesis via acyclic diene metathesis (ADMET) polymerization

Vajk Farkas[*1,2], Paul T. Anastas[3], Robert Tuba[1,3]

[1]*Institute of Materials and Environmental Chemistry Eötvös Loránd Research Network, Research Centre for Natural Sciences P.O. Box 286. Hungary*
[2]*Department of Organic Chemistry & Technology, Budapest University of Technology & Economics, Szent Gellért tér 4, Budapest, 1111, Hungary*
[3]*Yale Center for Green Chemistry and Engineering Yale University New Haven, Connecticut, 06511, US*
[*]*farkas.vajk@ttk.hu*

Keywords: biodegradable polymers, ADMET, olefin metathesis

Introduction.

Recently, polybutylene adipate terephthalate (PBAT), polybutylenesuccinate (PBS) and polybutylene carbonate (PBC) gain more and more attention as alternative biodegradable polymers for polypropylene (PP) and low-density polyethylene (LDPE).[1,2] The synthesis of these polymers via acyclic diene metathesis polymerization of diallyl esters and diallyl carbonate offer a less energy-intensive process compared to the traditional polycondensation method.

Commercially available, first-generation Grubbs catalyst (G1) had already been investigated in the past years. Ben-Haida and his co-workers reported that in the case of diallylterephtalate G1 was not able to reach high polymerization degree (PD) of 4 with molecular weight (M_w) of 1.0 *kDa* and polydispersity (PDI) of 1.25. In the case of diallyladipate, G1 showed slightly higher activity with PD of 7, M_w of 8.3, and PDI of 6.38.[3].

Results and discussion.

Newly synthesized cyclic (alkyl)(amino)carbene (CAAC) catalyst has been proven to be most efficient catalyst, when the polymerization was carried out in bulk with mechanical stirring at 75°C with 0.5 mol% catalyst load. Advanced polymer chromatography (APC) analysis showed acceptable molecular weight of the synthesized polymer. The unsaturated polymer can be hydrogenated at high pressure (20 bar) and high temperature (100°C) using 10% palladium on carbon.

Acknowledgments

The Authors are gratefull to Alexander von Humboldt - Stiftung for the financial support.

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Investigations into modulation of ZSM-5 acidity via modifier-assisted synthesis

M.H.Z. Faruqi[1], M. Kumar[1*]

[1]*Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi, India*
**manjeshkumar@chemical.iitd.ac.in*

Keywords: *Zeolite crystallization, ZSM-5, zeolite growth modifier (ZGM), zeolite acidity*

Introduction. ZSM-5 is a medium-pore silica-rich zeolite requiring high crystallization temperatures (423-473 K) and alkaline pH (>11) for synthesis. Acid sites in zeolite ZSM-5 are responsible for a variety of reactions such as conversion of methanol to gasoline/olefins, paraffin isomerization, etc [1]. Also, shape-selective catalysis in zeolites is achievable via modulation of crystal size and morphology to enhance exposure of certain crystal facets using zeolite growth modifiers [2]. Thus, tuning zeolite acidity along with modulation of crystal morphology is an interesting proposition for enhanced catalytic activity. Here, we present a novel approach to synthesize ZSM-5 with controllable acidity.

Experimental/methodology. The zeolite ZSM-5 was synthesized using hydrothermal method [3]. TEOS was added to a solution containing $NaAlO_2$ and TPAOH solution resulting in a dense gel formation. In the next step, a solution containing NaOH, TPABr, and deionized (DI) water was added. ZGM was added to the resulting mixture and stirred at room temperature for 20 hr, transferred to a Teflon-lined stainless-steel autoclave, and hydrothermally treated at 180°C for 48 hr.

Results and discussion. In this study, ZSM-5 crystal was synthesized by varying physicochemical growth conditions of mother liquor for zeolite synthesis before high-temperature hydrothermal treatment. The effect of monovalent and divalent salts on the morphological and acidity characteristics of the zeolite was investigated.

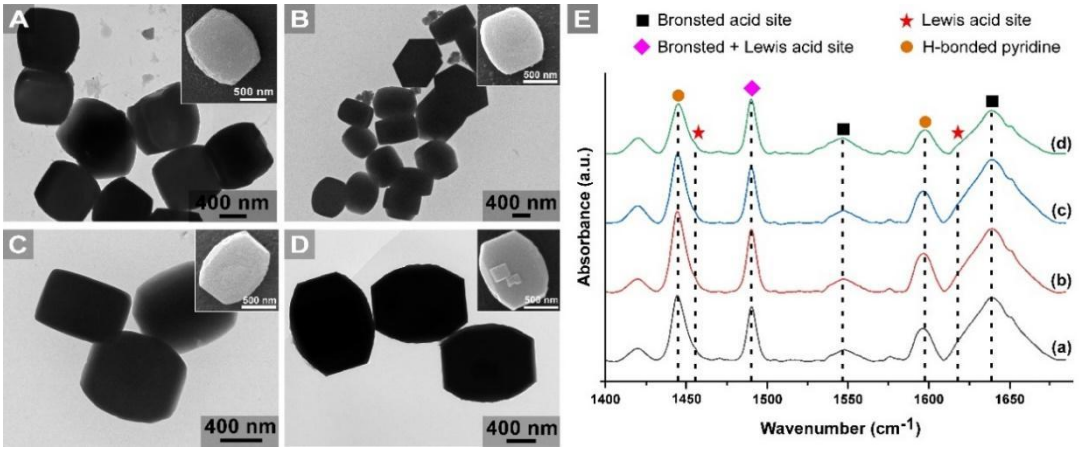

Figure-1: TEM and SEM (inset) images of synthesized ZSM-5 crystals showing twinned boat morphology in (A-D). (A) ZSM-5 control sample showed crystal size ~1.5 µm. (B) ZSM-5 synthesized in presence of Li^+ ions resulted in elongated (along c-axis) and faceted crystals with crystal size ~1.5-2 µm. (C) Presence of divalent Ca^{2+} ions during ZSM-5 synthesis resulted in crystal size ~1 µm. (D) Synthesis in presence of divalent Mg^{2+} resulted in uniform crystal size of ~1-1.5 µm. (E) represents IR spectra of pyridine adsorbed ZSM-5 samples in above order (A-D) for comparison of acidity characteristics.

The results indicated that, apart from affecting the particle size and morphology, growth modifiers can also be used to tune the acidity characteristics of zeolite ZSM-5. Significant changes in Bronsted and Lewis acidity were observed on switching between monovalent and divalent modifiers, which can be attributed to variable interaction of ions with framework and/or extra-framework constituents.

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Controlling the Crystallite Size and Polydispersity using Colloidal Silica Stabilizing Agent

Aditya[1], Manjesh Kumar[1*]

[1]*Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi, India*
[*]*manjeshkumar@chemical.iitd.ac.in*

Keywords: Catalysis, Stablizing agent, Growth modifiers, Polydispersity

Introduction. Tailoring the physical properties of advanced functional materials is crucial to ensure their superior performance for various applications. It requires a comprehensive understanding of their mechanistic pathways of formation [1],[2]. Here, we are investigating the industrially relevant zeolite, specifically SSZ-13, that has been used extensively in a myriad of applications such as selective catalytic reduction, Methanol to Olefin reaction, among others. Tuning the polydispersity, size, and morphology of the zeolite crystals has been a major challenge for efficient catalyst design. Owing to these challenges, we have designed a novel synthetic protocol to develop SSZ-13 crystals that can control the size, dispersity, and morphology of the particles. The approach uses economically viable modifiers that make the process commercially relevant. The SSZ-13 crystals were synthesized by modulating the physicochemical growth conditions of the mother liquor to produce crystals with varying size ranges and improved dispersity. We tracked the growth of crystallite under static and dynamic conditions using modifiers to develop the optimized particle size and distribution. To establish better control over the dispersity of particles, we investigated the effect of various salts (monovalent, divalent, trivalent) acting as counter ions or stabilizing agents on the growth dynamics of the mother liquor.

Experimental/methodology. The synthesis of SSZ-13 zeolite was carried out using the hydrothermal method[3]. NaOH was mixed with Deionized water followed by the addition of Structure Directing Agent (SDA), $Al(OH)_3$, LUDOX AS-40/HS-40, and the mixture were stirred for 2h at room temperature. This solution was then subjected to high-temperature hydrothermal treatment for 4-7 days in dynamic conditions.

Results and discussion. The conventional SSZ-13 crystals synthesized using the two silica sources produces a bimodal distribution of particles with size varying from nanometer to microns. It is desirable to synthesize the crystals with reduced polydispersity and smaller sizes for better catalysis. We explored the use of colloidal stabilizers here that are extensively used for obtaining stable LUDOX solutions namely Na^+ and NH_4^+ ions. Here, we show in figure 1 (A, B) control sample of SSZ-13 having bimodal particle distribution. In figure 1(C, D, E, F) shows that the additional rational design principle helped us to obtain a smaller (~260 nm) and larger crystal of 2 µm .The new synthesis protocol was able to achieve the monodisperse population. It is interesting to observe that particle morphology evolved from cubic shape to polyhedron (figure 1 E & F). We carried out detailed particle distribution analysis by volume and numbers to track the crystallization evolution which helped us to understand the growth phenomena. A comprehensive mechanism and complete library of particles were generated that will be presented during the conference. Our study presents a comprehensive picture of controlling particle attributes using mechanistic know-how.

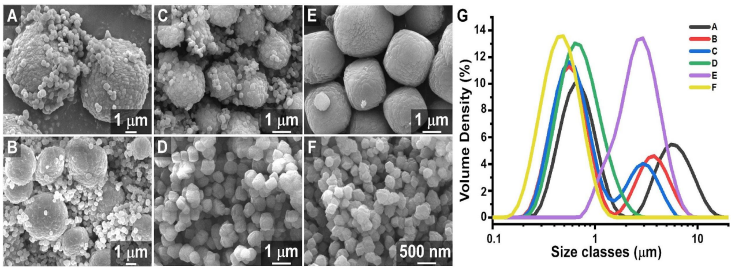

Figure 1: SEM images of the sample A)SSZ-13 control synthesized using LUDOX AS-40 B)control synthesized with LUDOX HS-40. C) Modifier 1 shows bimodal distribution like control samples. D) Modifier 2 shows mono-disperse particle with average size of ~520 nm E) Modifier 3 resulted in corrugated cubical particle with an average size of ~2 µm. F) Modifier 4 shows octahedral shaped particle with an average dimension of ~260 nm. G) Particle size distribution curve depicting the unimodal and bimodal distributions obtained by modifiers.

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Mechanochemical synthesis of Ru/CeO_2 catalysts for CO_x-free H_2 production from ammonia decomposition

A. Felli[1,*], M. Danielis[1], M. Zampol[1], A. Trovarelli[1], S. Colussi[1]

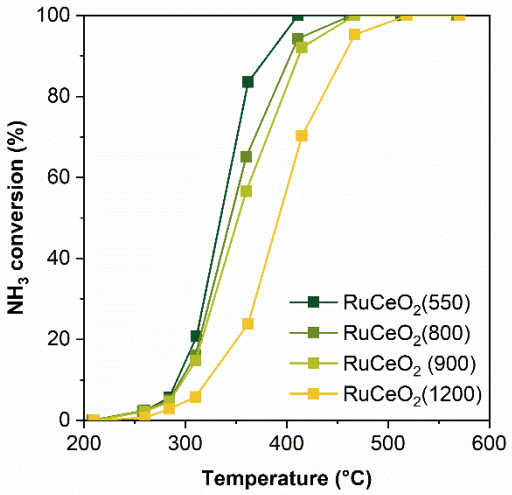
[1]*Dipartimento Politecnico e INSTM, Università degli Studi di Udine, 33100 Udine, Italy.*
[*]*felli.andrea@spes.uniud.it*

Keywords: Cerium oxide, mechanochemical synthesis, Metal-Support Interaction.

Introduction. Ru/CeO_2 is one of the most promising catalysts for the H_2 production from ammonia decomposition thanks to the chemical properties of cerium oxide and its interaction with Ru [1]. In this work, we studied Ru/CeO_2 catalysts prepared with a mild ball milling approach, which is a green, easy-to-do and fast method to prepare a solid catalyst [2]. For the first time, we evaluated the catalytic activity of milled catalysts towards NH_3 decomposition and we studied the parameters which could affect their performances, underlining the importance of the metal-support interaction (MSI) between Ru particles and CeO_2 support.

Experimental/methodology. Commercial CeO_2 (Rhodia) was calcined at different temperatures (550°C, 800°C, 900°C and 1200°C) for 4h (10°C/min) to evaluate the morphological properties of the supports. Ruthenium acetyl acetonate in powder form was milled with the different CeO_2 supports in a Pulverisette 23 Minimill for 20 minutes at 15 Hz (details reported elsewhere [2]) and calcined in air at 550°C for 2h. A conventional catalyst was also prepared via wet impregnation using CeO_2(550) as support. X-ray diffraction (XRD), N_2 adsorption, Temperature programmed reduction (TPR) and Raman spectroscopy were used for characterization. NH_3 decomposition was studied by loading 50 mg of sample in a tubular quartz reactor from RT to 550 °C exposed to 30 mL/min of 5% NH_3 in He monitoring gases by a micro gas chromatograph.

Results and discussion.



	BET S. A. (m^2g^{-1})	$I_{Ru\text{-}O\text{-}Ce}/I_{F2g(Ce)}$ (a. u.)	NH_3 conv. at 360 °C (%)
$RuCeO_2$(550)	115	0.14	83.5
$RuCeO_2$(800)	71	0.06	65.0
$RuCeO_2$(900)	35	0.05	56.9
$RuCeO_2$(1200)	4	<0.01	23.9

Left: NH_3 conversion for $RuCeO_2$(550), $RuCeO_2$(800), $RuCeO_2$(900) and $RuCeO_2$(1200). Right: surface area (SA), Metal-Support Interaction ($I_{Ru\text{-}O\text{-}Ce}/I_{F2g(Ce)}$) evaluation from Raman spectroscopy and NH_3 conversion at 360 °C for all the samples.

Light-off curves show an increase in catalytic activity for NH_3 conversion as SA increases; however, $RuCeO_2$(800) and $RuCeO_2$(900) show similar activity, despite having significantly different SA. In order to identify which parameter mainly affects the catalytic activity, we employed several characterization techniques to study the Ru/CeO_2 system. While XRD and TPR analyses show a qualitative difference in Ru dispersion among all the samples, Raman spectroscopy reveals that $RuCeO_2$(800) and $RuCeO_2$(900) possess an analogue Metal-Support Interaction, which could explain their similar performances despite a different SA. A more in-depth study to confirm the role of MSI between Ru and CeO_2 in ammonia decomposition is under way employing other characterization techniques.

Acknowledgments
Authors thank MUR and PON (CUP G25F21002600003) for funding.

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EMPOWERED CATALYST SUPPORTS

M Khasu[1], W Marquart[1], AJ Mayer[2], S Dann[2], SA Kondrat[2], M Claeys[1], N Fischer[1]

1. DSI-NRF Centre of Excellence in Catalysis c*change and Catalysis Institute, Department of Chemical Engineering, University of Cape Town, Cape Town, South Africa.
2. Department of Chemistry, Loughborough University, Loughborough, United Kingdom.

nico.fischer@uct.ac.za

Several industrial catalytic processes are currently being investigated as pathways to store renewable energy in chemical molecules in smaller decentralized plants. The whole family of processes is termed Power to X (PtX) with X representing the target molecule/product. While most of the processes within the PtX envelope are industrially established, the new boundary conditions of small-scale renewable energy-based plants can require a significant redesign of the catalytic materials to withstand the expected harsher reaction conditions. We have been focusing especially on the stability of promoters under reaction conditions and have developed a new design concept combining the physical structure of an oxidic support material with the provision of promotional functionality – empowered supports – and demonstrated this concept in the iron-based Fischer-Tropsch synthesis (FTS).

The exact speciation of promoter elements in classic catalysts under reaction conditions is still not fully resolved. Low concentrations and promoter mobility [1] present the most significant challenges in this regard. Without a clear understanding of the interaction between the promoter and the active phase, catalyst optimization through design is not possible. Innovative preparation techniques have shown that when an intimate contact between the active phase and the promoter is achieved, the promoting effects observed surpass effects reported for catalysts prepared with conventional impregnation approaches [2].

Based on a rhombohedral $LaAlO_3$ perovskite, a series of supports was synthesized, partially replacing La with K and Al with Mn. Extensive laboratory and synchrotron-based characterization was conducted to ensure that the promoter elements are indeed incorporated in the perovskite structure. Iron oxide nanoparticles were subsequently deposited on these materials. Following a reductive treatment in hydrogen at elevated temperatures, the activity of the catalysts under FTS reaction conditions was investigated.

A combination of XRD, TEM and XAS confirmed the success of the perovskite synthesis. When Mn is present, the average oxidation state of Mn is elevated, countering the charge imbalance induced by the replacement of La^{3+} with K^{+}. Reductive treatment reduces the average oxygen coordination of the La site from 12 to 11 stabilizing K^{+}, especially in $La_{0.9}K_{0.1}AlO_3$.
While iron supported on $LaAlO_3$ showed no enhanced activity or selectivity compared to conventional supports, the presence of K in the perovskite structure significantly enhances CO conversion. To achieve a comparable conversion, the space velocity had to be increased by a factor of 3.75. Under these conditions, the promoted catalyst displays a lower methane selectivity and enhanced chain growth as well as a much higher olefin to paraffin ratio in the hydrocarbon product. The CO_2 selectivity, the product of the water-gas shift reaction (WGS), is only slightly increased. The addition of small amounts of Mn further reduces methane and CO_2 selectivity while maintaining the high olefin to paraffin ratio. Higher Mn contents are detrimental to the CO conversion and increase the yield of short chained hydrocarbons. Compared to iron supported on $LaAlO_3$ promoted conventionally via potassium impregnation, the here developed materials have a much lower C1 product fraction, predominantly due to the decoupled enhancement of the FTS and the WGS reaction by the potassium incorporated in the perovskite structure compared to potassium species obtained through impregnation.

We have no reason to believe that the here described effects represent a singularity for the chosen promoters and the FTS but expect that this new catalyst design concept can also be applied to and improve various industrially relevant promoter dependent catalytic processes such as the Haber-Bosch synthesis.

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The effect of variation in support porosity for supported catalytically active liquid metal solution catalysts

A.L Folkard[1,2*], N. Madubuko[1], N. Taccardi[1], M. Haumann[1], H.B Friedrich[2], P. Wasserscheid[1]

[1]*Friedrich-Alexander Universität Erlangen-Nürnberg, Erlangen, Germany*
[2] *University of KwaZulu-Natal, Durban, South Africa*
[*]*213557335@stu.ukzn.ac.za*

Keywords: Alloys, mesopores, macropores, Sol-gel, supported catalysts, template-free

Supported catalytically active liquid metal solution (SCALMS) catalysts have shown promising results in improving activity and longevity for dehydrogenation and oligomerization reactions.[1, 2] In SCALMS catalysts, small amounts of an active metal (e.g. Pt, Rh, Ni, Pd) are dissolved in a low melting metal (in this case Ga) matrix, resulting in liquid alloys at reaction conditions. The unique reactivity and catalytic performance of SCALMS is attributed to the presence of its highly active and dynamic single active sites at the metal-gas interface. In literature, it has been shown that this interface, determined by the Ga droplet size, is an important component that is affected by surface morphology and roughness.[1, 3]

Often an overlooked component of catalyst design, this contribution explores novel synthesis routes for γ-Al_2O_3. γ-Al_2O_3 is a structural polymorph of alumina which has a wide range of applications in catalysis as either an active phase or support. By designing supports with ideal uniform, rough surfaces of defined morphology, the next generation of tailored SCALMS can be achieved. Our approach to γ-Al_2O_3, using novel template-free glycothermal and sol-gel methods, creates supports of varying porosity profiles. This contribution will discuss the location (**Fig. 1)** of the decorated Ga droplet relative to the various γ-Al_2O_3 pore networks and explore which pore size range is best suited to the next generation of SCALMS catalyst.

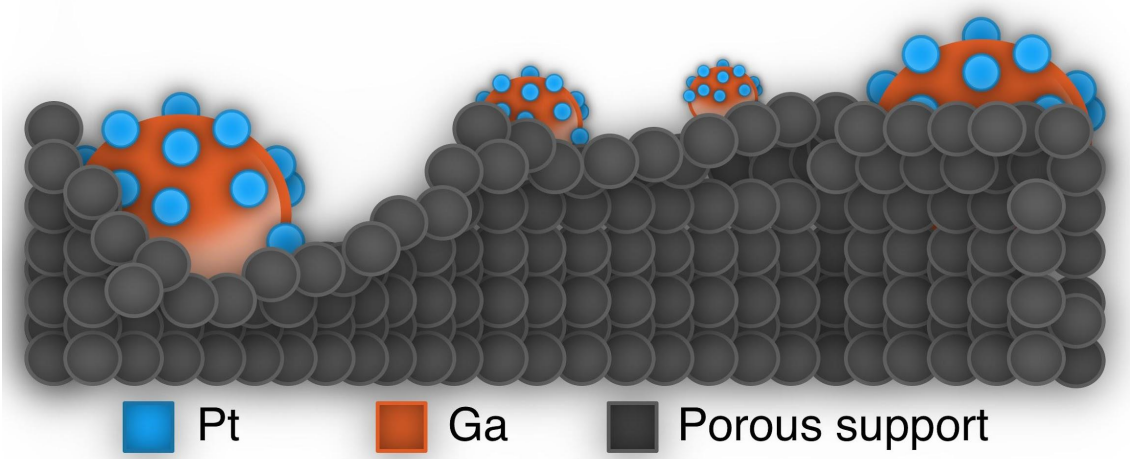

Figure 1: A visualization of Pt decorated Ga droplets on the surface of a porous support.

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Effect of ball-milling operational parameters on the chemistry and morphology of CeO_2 powders

Maila Danielis*, Andrea Felli, Nicolas Fonda, Sara Colussi, Alessandro Trovarelli

Polytechnic Department and INSTM, University of Udine, Via del Cotonificio 108, 33100 Udine (Italy)
**maila.danielis@uniud.it*

Introduction. The mechano-chemical activation of powder materials represents an interesting opportunity for the sustainable functionalization of heterogeneous catalysts [1,2], by inducing meta-stable phase transformations on metal oxides [3,4] or promoting unique metal-support interactions on supported metal catalysts [1,5]. Here, the simple mechanical action on pure CeO_2 supports was investigated in terms of textural, morphological and redox properties, as a function of starting material and milling intensity, allowing for the prediction and design of CeO_2 powders properties for catalytic applications by dry milling.

Experimental/methodology. Different CeO_2 powders were obtained from commercial ceria (Rhodia) by calcination in static air at 550°C, 900°C, 950°C and 1200°C. Then, the powders were milled at mild (ME) and high (HE) energy milling conditions, for times ranging between 0.5 and 8 hours, and their morphological, textural and redox properties were followed by means of N_2 adsorption isotherms, X-ray diffraction (XRD), dynamic laser scattering (DLS), Raman spectroscopy and and H_2 reduction (TPR). The redox activity was evaluated in CO oxidation tests under 2%CO, 5%O_2 in N_2, at a GHSV≈80000 h^{-1}.

Results and discussion. Under mild energy milling, variations of the initial properties of the CeO_2 powders are observed only at long (> 2h) milling times (not shown) while the most significant changes in CeO_2 redox and morphological properties are achieved by high energy milling. Most noticeably, the surface area of ceria powders tends to an equilibrium value (Fig.1a), due to crystallite breakage being induced on larger particles and agglomeration promoted on smaller particles [1]. Simulaneously, the mechanical action generates defects on the ceria surface [4,5], highlighted by the appearance of a Raman band at 600 cm^{-1} (Fig.1b). Despite reduction in surface area (Fig.1a) and porosity (not shown), the increased amount of surface disorder leads to enhanced redubility at low temperatures (>500°C, Fig.1c), which leads to improved catalytic performance in reaction where oxygen exchange is required and could potentially act as anchoring points for metals when used as a support oxide.

Figure 1. BET surface area (a), Raman spectra (b) and H_2 consumption below 500°C (c) as a function of milling time at high energy for selected samples.

Acknowledgments
The authors acknowledge MUR, REACT EU – PON 2014-2020 and PNRR iNEST programs for funding.

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A chemo-enzymatic oxidation cascade to activate C–H bonds with in situ generated H_2O_2

D. R. Ford, R. J. Lewis and G. J. Hutchings
Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, Translational research hub, Cardiff University, 4 Blackweir Terrace, CF10 3EY, Cardiff, UK FordDR@cardiff.ac.uk

Key words: AuPd, hydrogen peroxide, non-specific peroxygenase, cascade, oxidation.

Introduction. The evolved non-specific peroxygenase enzyme from *agrocybe aegerita* (PaDa-I variant) is demonstrated to be highly selective for hydroxylation reactions of C-H groups, only requiring a continuous low-level quantity of H_2O_2 to function. Supported AuPd nanoparticles shows great promise in fulfilling this requirement, utilising H_2 and O_2 gas to produce a continuous stream low concentration H_2O_2 in a one-pot oxidation cascade.
Experimental/methodology. 1%wtAuPd /TiO_2 catalysts were prepared by an excess-chloride co-impregnation procedure.[1] Chemo-enzymatic cascade reactions were performed in a one-pot system under conditions that maintain enzyme stability.
Results and discussion. Chemo-catalysed H_2O_2 synthesis (Figure 1a (black squares)) in absence of enzyme was determined, showing sufficient production for enzymatic reactions to occur. Assessment of the enzyme-mediated activation of C-H bonds was carried out via hydroxylation of cyclohexane (Figure 1a), ethylbenzene (Figure 1b) and isophorone (Figure 1c) in the tandem enzymatic/catalytic reaction. Through optimisation of the process, total turnover numbers may be reached which rival current state-of-the-art co-enzymatic systems. We consider that this chemo-enzymatic approach has potential for a wide range of applications in tandem reactions due to the ease of adaptation into current reactor technology and infrastructure, lower energy input as there is not requirement for illumination compared to recent photocatalytic approaches and inherent efficiency of the process in only producing water as a byproduct without the requirement for organic molecules such as MeOH as a supply of electrons. The nature of the catalyst materials as both effective hydrogenation and oxidation catalysts significantly extends the scope of the reaction cascades that can be considered and can open the pathways to efficient tandem heterogeneous/biocatalytic processes.

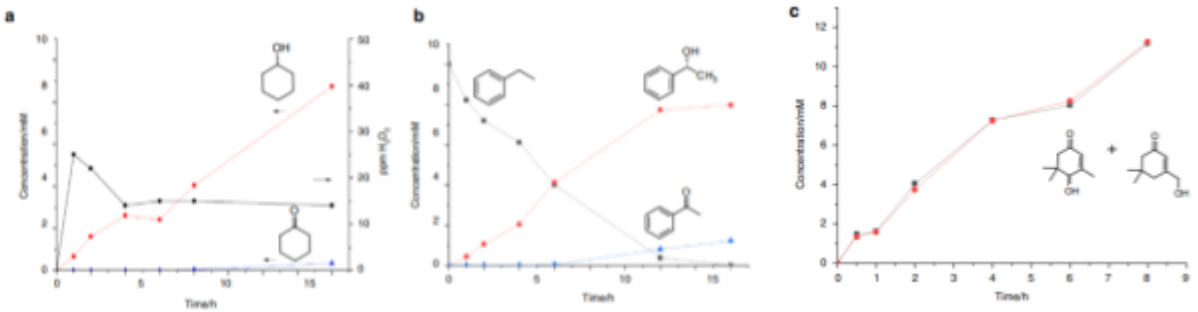

Fig. 1 Time-on-line hydroxylation reactions of a H_2O_2 production (black squares) (in the absence of enzyme) and cyclohexane oxidation to cyclohexanol and cyclohexanone b Ethylbenzene oxidation to 1-phenylethanol c Isophorone oxidation to 4 and 7-hydroxyisophorone.

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Immobilisation of activated carbons in αAl_2O_3 membranes by click chemistry for advance catalytic oxidation

C. Freitas[1*] and O. J. P.S Sousa [1]

INL-Iberian Nanotechnology Laboratory, Avenida Mestre José Veiga, 4715-330, Braga, Portugal
[*]catia.freitas@inl.int

Keywords: Water treatment, microporous ceramic membranes, click chemistry.

Introduction. Water is a valuable resource, crucial to all living organisms and multiple human activities, such as domestic uses, agriculture and industry. However, several emerging organic pollutants end up in vital aquatic compartments, such as surface water, groundwater and even drinking water. The appearance of these pollutants has been discovered at all stages of resource management systems and their negative impact on human and environmental health has become increasingly evident, even when found in trace concentrations [1]. However, both traditional treatments and the most advanced technologies available are ineffective in the removal of these micropollutants.

The aim of the SmartOxidation project is the use of catalytic ozonation in the presence of catalysts immobilised on microporous ceramic membranes for the creation of a unique solution leading to the removal of emerging organic pollutants and allowing the reuse of the wastewaters. Carbon materials, especially in powder form, have already been proven suitable for advanced oxidation treatment processes [2] due to their unique textural and superficial properties that can easily be modified. Microporous ceramic membranes are an interesting support for carbons materials owing to their high thermal, mechanical and chemical stability, high hydrophilicity, porosity and resistance to ozone. Additionally, the combination of these two materials leads to an increase in effluent flow and prevents biofouling. Our goal is the development of new ultra-thin film composite membranes and the study of their behaviour for catalytic ozonation.

Experimental/methodology. The strategic designing and synthesis are performed via click chemistry to achieve high interfacial adhesion between the support and the catalytic material by adding an azide moiety-containing material with an alkyne-functionalised phase. The design is done with activated carbons with high surface area and αAl_2O_3 membranes with conical and parallel pores, both materials modified prior to the functionalisation with azide and alkyne groups to activate their surface and to enhance their catalytic behaviour. This approach allows fast-rate reactions with high chemical yields using non-toxic solvents, simple reagents and straightforward reaction conditions.

Various characterisation techniques including Fourier transform infrared spectroscopic (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray spectrum (EDX) and N_2 physisorption were used to ascertain the successful functionalisation of the materials.

Results and discussion. The results demonstrated the incorporation of high amounts of azide and alkyne groups in both αAl_2O_3 membranes and activated carbons. In addition, the XPS results suggested the incorporation of a homogeneous population of the azide groups on the surface with a better vertical orientation, which is more accessible and reactive for click reaction.

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Imidazolium-based hypercrosslinked ionic polymer as metal-free catalyst for *N*-formylation of amines with CO_2 and Phenylsilane

Beatriz Fuerte-Díez, Elizabeth Rangel-Rangel, Marta Iglesias, Eva M. Maya

Instituto de Ciencia de Materiales de Madrid. CSIC, C/ Sor Juana Inés de la Cruz, 3, 28049, Spain

**b.fuerte.diez@csic.es*

Introduction. The utilization of CO_2 as a raw material for the synthesis of chemicals is an opportunity to convert a harmful gas for the environment into an added-value compound. Formamides can be prepared from CO_2 and are an example of versatile chemicals [1]. The use of an ionic liquid as metal-free catalyst for this reaction has gained great interest since it allows the reaction to be carried out in mild conditions: room temperature and moderated CO_2 pressure [2]. We present a supported ionic-based catalyst prepared by Friedel-Crafts type reaction, by reacting biphenyl and 1-benzyl-3-methylimidazolium chloride (BzmimCl) and its performance as heterogeneous catalyst in the formylation of amines to obtain formamides.

Experimental. The catalyst HCP-BzmimCl was obtained by reaction of biphenyl (0.37 mmol) and BzmimCl (1.5 mmol) in DCM under inert atmosphere in the presence of $AlCl_3$ (16.04 mmol) as catalyst at 50°C for 48 hours. The solid was isolated by filtration, washed with HCl 0.005 M, water and then purified by Soxhlet extraction with methanol.

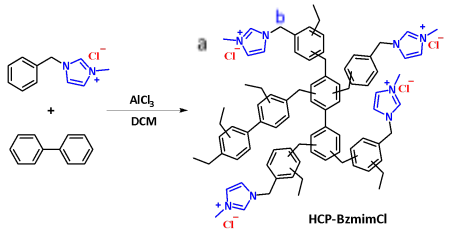


Figure 1. Synthesis of HCP-BZmimCl

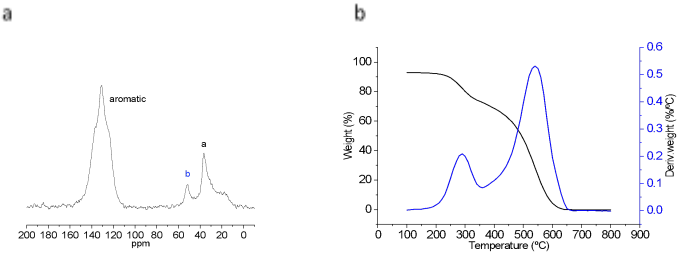


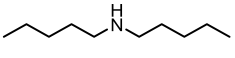
Figure 2. ^{13}C-NMR (a) and TGA (b)

Results and discussion. The ^{13}C-NMR HCP-BzmimCl shows the characteristic signal attributed to the methyl groups of the imidazolium and to the methylene groups (Figure 2a). The thermogravimetrical analysis (TGA) (Figure 2b) indicated thermal stability with an initial degradation temperature close to 300°C. The elemental analysis showed the incorporation of two units of BzmimCl per biphenyl group.

HCP-BzmimCl results an effective catalysts for N-formylation of amines with CO_2/$PhSiH_3$ (table 1). Whith a 10mol% catalyst a conversion of 75% (50% selectivity) was obtained (entry 1), if a 20mol% catalyst was employed we obtained selectivily the formamide (entry 2). The addition of 2 mmol of DMF to the reaction mixture reduces considerably the reaction time (entry 3) because it activates Si-H and N-H bonds. A control experiment in the absence of catalyst confirms that it is essential to obtain acceptable yields and selectivities (entries 4 and 6). With N-methylaniline as susbtrate, the product is selectively obtained but in lower yield (entry 5). The catalyst can be reused at least for 5 cycles maintained their structure.

Table 1. Synthesis of formamides from amines and CO_2 using HCP-BzmimCl as catalyst. [a]



Entry	amine	Time (h)	Additive (mmol)	Conv. (%)	Select. (%)
1		24	none	75	50
2[b]		24	none	85	100
3		4	DMF (2)	100	100
4[c]		4	DMF (2)	40	100
5		6	DMF (2)	60	99
6[c]		6	DMF (2)	5	50

[a] $PhSiH_3$ (1 mmol), HCP-BzmimCl (10%), P (CO_2) = 5 bar, T = 35°C [b] HCP-BzmimCl (20%) [c] Without HCP-BzmimCl

Acknowledgments *This work was supported by the project CATCO2NVERS funded by the European Union´s Horizon 2020 research and innovation program under grant agreement No 101000580.*

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Synthesis and Catalystic Application of Bifunctional Composite Catalysts between Supported Metal Nanoparticles and Polyoxometalates

S. Fukuda[1], S. Kikkawa[1], R. Takahata[2], K. Suzuki[3,4], K. Yamaguchi[3], T. Teranishi[2], S. Yamazoe[1,4*]

[1]*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Tokyo, Japan*
[2]*Institute for Chemical Research, Kyoto University, Kyoto, Japan*
[3]*Department of Applied Chemistry, School of Engineering, The University of Tokyo, Tokyo, Japan*
[4]*Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency, Tokyo, Japan*
**E-mail: yamazoe@tmu.ac.jp*

Keywords: Supported metal nanoparticles, Polyoxometalate, Bifunctional catalyst

Introduction. The designs of the metal nanoparticle surfaces and metal-metal oxide interfaces are important for developing efficient hydrogenation catalysts. Recently, composites of Au nanoparticles (NPs) with metal oxide clusters (polyoxometalate, POM) as a protective ligand have been reported[1)]. We have reported that Lindqvist-type POMs composed of group V elements, $[Nb_6O_{19}]^{8-}$(Nb6) and $[Ta_6O_{19}]^{8-}$(Ta6), exhibit strong base catalytic activity due to the high local negative charge of the surface O site[2)]. In this study, the basic POMs were modified on the surface of Al_2O_3-supported AuNPs by a simple adsorption method (Fig. 1), and the Au NPs catalysts with Au-POM interfaces were applied to the hydrogenation of aromatic nitro compounds.

Fig. 1. POM-modified Al_2O_3-supported Au NPs.

Experimental. Al_2O_3-supported Au nanoparticles were prepared by the impregnation method. NaOH aq. Was added to 10 mM $HAuCl_4$aq. up to pH=9 and then Al_2O_3 was suspended in the solution (Au/Al_2O_3). Au/Al_2O_3 was dispersed in aqueous solutions of POM ($K_8Nb_6O_{19}$, $K_8Ta_6O_{19}$, and $K_8SiW_{11}O_{39}$)in excess of Au content. After vacuum-drying at 333 K for 2 h, POM-modified Au/Al_2O_3 (Nb6-Au/Al_2O_3, Ta6-Au/Al_2O_3, and SiW11-Au/Al_2O_3) was obtained. Catalytic hydrogenation of *p*-nitrophenol (*p*-NP), nitrobenzene (NB), or p-nitrostyrene (*p*-NS) was performed in an autoclave (catalyst: 5 mg, substrate: 62.1 μmol, methanol: 1 mL, H_2: 1 MPa, reaction temperature: 353 K, reaction time: 2 h).

Results and discussion. STEM-EDX analysis and ICP measurement indicated that the surface of the Au NPs (2.7 nm ± 2.0 nm, 0.68 wt%) were decorated with $[Nb_6O_{19}]^{8-}$ or $[Ta_6O_{19}]^{8-}$ (8.0 or 18 mmol/g_{cat} as the polyoxometalates). Nb K- and Ta L_3-edge XAFS spectra showed that the Lindqvist structure of $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$ maintained their structures after modification.

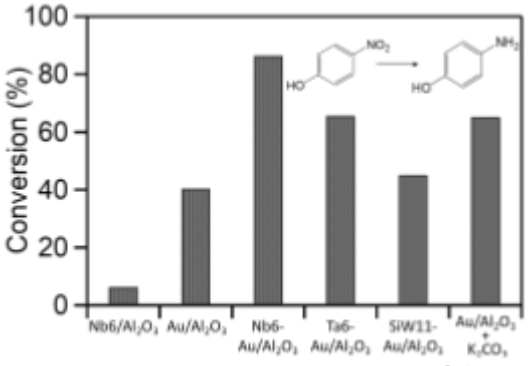

Fig. 2 Conversion p-NP over POM-Au/Al_2O_3.

Fig. 2 shows the conversions of p-NP over the POM-modified Au/Al_2O_3. The catalytic activity of Au/Al_2O_3 was significantly enhanced by modification with $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$, whereas $[SiW_{11}O_{39}]^{8-}$ modification did not enhance the activity. $[Nb_6O_{19}]^{8-}$-adsorbed Al_2O_3 (Nb6/Al_2O_3) hardly showed activity. The reaction proceeded with Au/Al_2O_3 when K_2CO_3 was added as a base, suggesting that the base plays a crucial role in the reaction. In addition, the modification with $[Nb_6O_{19}]^{8-}$ increased the conversion of NB and p-NS in their hydrogenation reactions. In summary, we have developed a composite catalyst with AuNPs and POM that drove the efficient H_2 activation at the AuNPs-POM interface, and the cooperation of the reduction activity of AuNPs and base catalytic activity of $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$ resulted in the efficient hydrogenation activity of p-NP[3)].

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Synthesis of heterogeneous catalysts by gliding arc plasma

F. Hanon*, E. M. Gaigneaux**

UCLouvain, Institute of Condensed Matter and Nanosciences (IMCN), Louvain-la-Neuve, Belgium
** fanny.hanon@uclouvain.be; ** eric.gaigneaux@uclouvain.be*

Introduction: Glidarc plasma (GP) is an ecologic and economic promising technique for the synthesis of catalysts with interesting properties (TiO_2, SnO_2, MnO_2, FeO_x) [1,2]. The addition of a post-discharge (PD) step in the synthesis of some of them (MnO_x, FeO_x) has also improved their characteristics (higher specific surface area and catalytic activity) (Fig.1) [2,3]. In the literature, it is suggested that the reason why metallic precursors form precipitates during the discharge and why the formed solid is transformed during the PD is mainly due to the principal species generated (OH°, NO°, H_2O_2, HNO_3, HNO_2). However, these hypotheses were never proven before. The aim of our research is therefore to understand how the synthesis of catalysts by GP works and how the method could be improved.

Methodology: The radicals generated in the GP can induce the precipitation of the corresponding (hydr)oxides of metal precursors solutions exposed to the discharge. The formed suspension is either subjected to a PD step at a certain temperature for a certain time or is direclty centrifugated. The recovered solid is then dried and calcined to obtain the final catalyst (Fig.1).

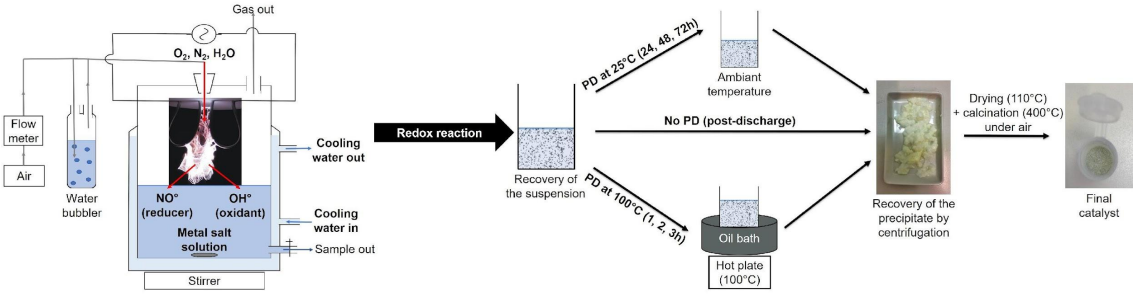

Fig.1: Scheme of the GP reactor and methodology for catalysts synthesis by GP

Results and discussion: The factors that impact the ability of a precursor to react by GP were first identified. These parameters are, among others, the acidification of the medium during the discharge due to the formation of HNO_3 and HNO_2, the oxidation state of the precursor and its capacity to react spontaneously with water, and the types of species formed thanks to the carrier gas. Indeed, contrary to the majority of the precursors that do not form solids by GP (Ni, Bi, ...), all precipitating metal salts are able to form a metal or (hydr)oxide at low pH. Moreover, among the precursors reacting by GP, some are spontaneously but slowly oxidized/reduced to (hydr)oxides in water ($KMnO_4$, $TiCl_3$, $Fe(SO_4)_2$, $(NH_4)_2Fe(SO_4)_2$) and others are hydrolyzed before reacting with the plasma species ($HAuCl_4$, $SnCl_2$, $SnSO_4$). Finally, depending on the type of carrier gas used (N_2, Ar, O_2), the precipitation of precursors reacting by humid air GP does not always take place, demonstrating the importance of some species on the reaction.

It will also be shown that the PD is a thermal and temporal maturation stage where the species formed during this step have no effect on the way the solid changes. Hence, the thermal effect of the PD could be reproduced directly during discharge by removing the cooling system during the exposure. Under these conditions, solids with similar characteristics to those obtained in PD (higher specific surface area and catalytic activity) were developed but much faster. For example, SnO_2 synthesized from $SnCl_2$ by GP is catalytically more active when a PD step is performed but is even more active if the exposure is done without the cooling system (Fig.2).

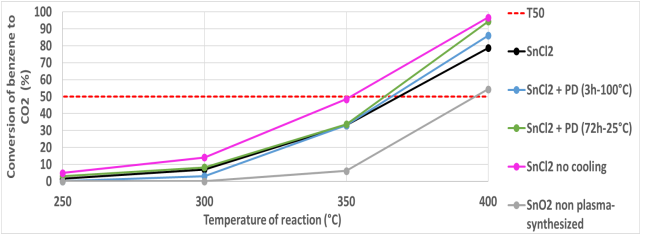

Fig.2: Conversion of benzene to CO_2 as a function of the temperature of reaction of SnO_2 synthesized from $SnCl_2$

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A highly activating electron-rich phosphasilinane ligand for Pd catalyzed C-X coupling reactions

Dr. Detlef Gaiser[1], *Dr. Michael Gock*[1], *Sabrina Kräh*[2], *Prof. Dr. Oliver Trapp*[2]

[1]*Heraeus Precious Metals, 63450 Hanau, Germany*

[2]*Ludwig-Maximilians University, Munich/Germany*

Coupling reactions play an important part in the syntheses of sophisticated active ingredients for pharmaceutical, agro- and fine-chemistry. These reactions have become an essential tool in drug synthesis and design. Many of these coupling reactions run with the help of homogeneous palladium phosphine catalysts. Highly influential for the conversion of a specific substrate is the use of the right ligand. Years of research have proven that effective biaryl phosphane (Phos) ligands are very effective choice in many cases. However, heteroatom-containing substrates strongly influence these reactions, as they complicate the coupling due to their competitive coordination to the palladium catalyst and different electronic structure.[1] As a consequence, previous Phos ligands only achieve good yields at high temperatures and long reaction times. We present here a highly active Phos ligand (SabPhos) that supplies excellent yields for C-N coupling reactions at ambient temperature. A silicon containing phosphane provides a pyramidal structure of the phosphorus while reducing steric hindrance. In palladium catalyzed reactions, this ligand rapidly couples a broad range of heteroaryl chlorides via C-C bonds with boronic acids and C-N bonds with secondary amines in high yields under mild conditions.[2]

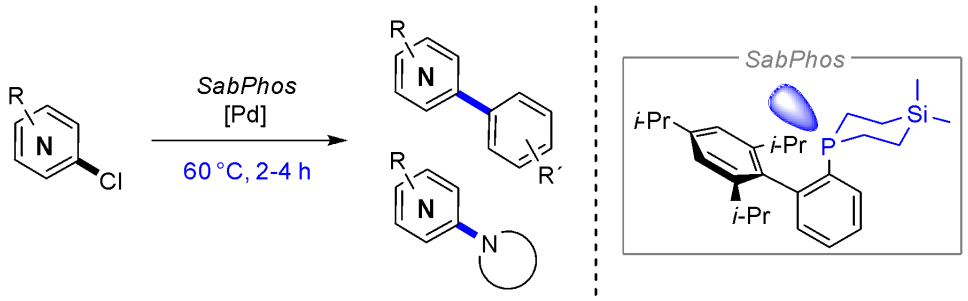

Figure: SabPhos Ligand enables effective palladium catalyzed C-X bond formation of heterocycles under mild conditions.

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Surface nickel complexes as models for heterogeneous oligomerization catalysts

S. Aïssiou[1*], N. Merle[1], M. Sauthier[1]
[1]*Unité de Catalyse et Chimie du Solide—UMR CNRS 8181, Univ. de Lille, 59652 Villeneuve d'Ascq, France*
[*]*samy.aissiou@univ-lille.fr*

Keywords: Sustainable fuels, oligomerization of olefins, nickel, surface organometallic chemistry

Introduction.

Since the development of sustainable processes for light olefin production (ethanol dehydration, CO_2-to-light-olefins), oligomerization has become relevant for the production of sustainable fuel. But while nickel has already proven to be efficient in homogeneous oligomerization (SHOP, Dimersol), industrial processes using heterogeneous nickel-based catalysts are still rare [1]. Also, on a mechanistic point of view, the nature and formation of the active sites remain elusive. In order to answer to these questions, nickel-based model catalysts have been synthesized using surface organometallic chemistry (*SOMC*). This methodology gives access to well-defined supported species and has been successfully used for various applications including the synthesis of well-defined, efficient metathesis catalysts [2].

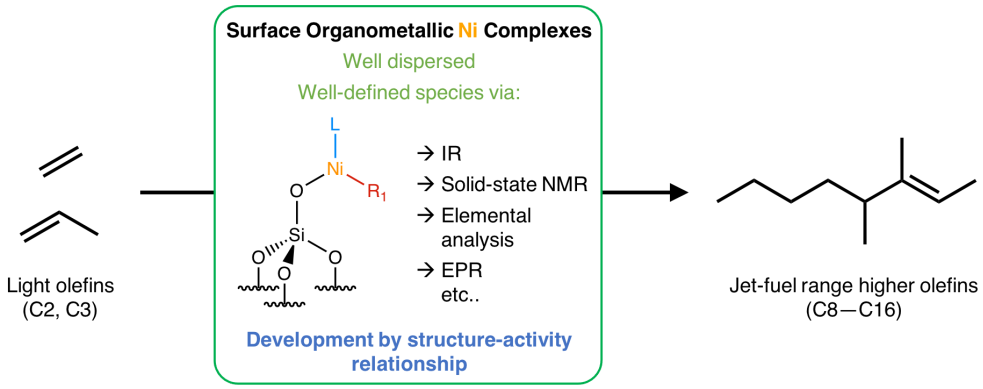

Fig 1. Well-defined supported catalysts as models for the oligomerization of light olefins into sustainable jet-fuel

Experimental/methodology.

Model catalysts have been synthesized by reacting organometallic nickel complexes with surface silanol groups on a variety of supports (SiO_2 or SiO_2-Al_2O_3 of various Si/Al ratios). Thermal treatment of the supports allows to obtain well-dispersed nickel complexes. Catalysts are characterized via IR (DRIFT), solid-state NMR, EPR, and elemental analysis. A tubular fixed bed reactor is used to investigate how pressure, temperature and olefin flow rate affect the selectivity/activity of each different compound.

Results and discussion.

Infrared analysis as well as elementary analysis both indicate successful chemical grafting (creation of a nickel-oxygen bond between metal support) of a variety of complexes. Solid-state ^{1}H and ^{13}C NMR experiments show that on highly dehydroxylated silica (pure amorphous silica treated at 700 °C) at least two, closely related surface species are formed. EPR experiments suggest that one the species at least is paramagnetic. Preliminary catalytic experiments have confirmed the activities of such catalysts in ethylene oligomerization, and their performances are compared to those of a classical heterogenous catalyst.

Acknowledgments
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Insights of the Ru exsolution from $La_1Fe_{0.9}Ru_{0.1}O_3$. Catalysts for propane combustion

Jaime Gallego[1,2], Yu Wang[1,3], Herbert Over[1], Bernd Smarsly[1]

[1]*Physikalisch-Chemisches Institut, Justus Liebig University, Heinrich-Buff-Ring 17, D-35392 Giessen, Germany*
[2]*Center for Materials Research, Justus Liebig University, Heinrich-Buff-Ring 17, D-35392 Giessen, Germany*
[3]*Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, PR China*

[*]*jaime.gallego-marin@phys.chemie.uni-giessen.de*

Keywords: Exsolution, Heterointerface, Perovskite oxides, Oxidation reaction, Surface reconstruction

Introduction. Heterointerfaces (Nanoparticles/support) obtained through exsolution have shown extraordinary performance compared to conventional impregnation. During the exsolution, one or various elements of a mixed oxide are brought to the surface due to applied stress creating partial socketed nanoparticles. These exsolved platforms have shown extraordinary performance for catalytic reactions such as water splitting, oxygen reduction, and thermal oxidation, among others. In this work, we rationally investigated the evolution of an exsolved Ru-surface, which will allow us to design and control these catalytic systems, also containing other different elements.

Experimental/methodology. We prepared $La_1Fe_{0.9}Ru_{0.1}O_3$ oxide through a sol-gel method with a final calcination temperature of 750 °C. Ru was exsolved under H_2 at 800 °C to obtain the heterointerface $Ru_{Exsolved,\ NPs}/La_1Fe_{0.9}Ru_{0.1-x}O_3$. Propane thermal oxidation was used as a catalytic test to understand the surface reactivity during the different steps. TEM, EDX, XPS, and XRD were the main characterization techniques used to trace the material transformations.

Results and discussion. Conventionally, ruthenium present 4+ as an oxidation state when forming oxides, RuO_2. However, Ru exhibits other oxidation states in different compounds. Through XPS, we found that Ru is mainly present as 3+ after calcination. The presence of Ru^{3+} proves that Ru substituted Fe into the perovskite-like structure in which, in its stoichiometric form, B-site presents mainly 3+ as oxidation state. After exsolution, Ru^0 appeared, indicating the formation of NPs on the surface. We also detected Ru^{4+} and assigned it to oxidative passivation of the metal under air when the sample was prepared and transferred for the XPS analysis. XRD showed that the perovskite-like was obtained and preserved after exsolution. Combining these characterization results and the catalytic tests, we were able to track the surface evolution during the different treatment steps and after the catalytic test. These changes are summarized in **Figure 1**.

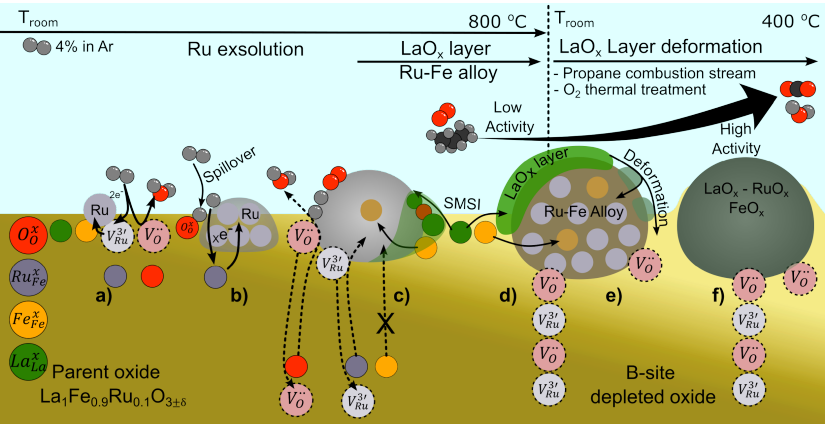

Figure 1. Schematic surface evolution of the $La_1Fe_{0.9}Ru_{0.1}O_3$ perovskite-like oxide. Under hydrogen atmosphere, a redox reaction takes place, oxidizing the H_2 to form H_2O and transferring electrons to the surface, obtaining metallic Ru atoms (a). This process creates oxygen and ruthenium vacancies and metallic ruthenium over the surface, which are nucleation points for growing metallic nanoparticles (b). At the same time, the exsolution goes ahead with increasing the temperature. At higher temperatures (>500 °C), Fe from the near surface can exsolve into the Ru nanoparticles, forming $Ru_{Enriched}$-Fe alloy and letting a $LaO_{x\text{-enriched}}$ surface (c). Thus, in accordance with the SMSI phenomenon, LaO_x species migrate along the metallic surface to cover them entirely (d) at high temperatures (800 °C). This LaO_x overlayer negatively affects the catalytic activity for propane combustion. However, we found that the catalytic activity increases significantly after the first reaction cycle or oxidation treatment (400 (C). This change was attributed to a surface reconstruction (e), cleaning the NPs surface, and transforming them in a mix of $Ru_{Enriched}$ – Fe – La oxides (f).

Metal phosphide nanoparticles for the hydrotreatment of methyl laurate

D. García Pérez[1*], M.C. Álvarez Galván[1], J.M. Campos Martín[1*], M.C. Capel Sánchez[1], S. Habas[2]

[1]*Instituto de Catálisis y Petroleoquímica (CSIC), Madrid, Spain.*
[2]*National Renewable Energy Laboratory, Colorado, USA.*
[*]***Corresponding Author** diana.garcia@csic.es*

Introduction.

Transition metal phosphide nanoparticles (NPs) are a promising active phase for hydrotreatment processes because of their advanced catalytic properties that result from a combination of metallic and acidic surface sites. This work aims to test the activity of catalysts based on NPs phosphide supported on silica in the hydrodeoxygenation of methyl laurate (a model compound for vegetable oil) to produce green liquid fuels.

Experimental/methodology.

$Ni_{1.6}Mo_{0.4}P$ and Ni_1Mo_1P nanoparticles (NPs) were first synthesized by a facile molecular precursor route [1]. The NPs were incorporated into silica support. A reference MoP/SiO_2 catalyst was prepared by the direct reduction phosphite method [2]. Prepared NPs and catalysts were characterized by chemical analysis, XPS, TEM, and XRD. The prepared catalysts were tested in the hydrodeoxygenation (HDO) of methyl laurate to hydrocarbons. The reaction was performed at two different liquid space velocities (LHSV= 6 or 3 mL/g/h), and temperatures (300 or 350 ºC).

Results and discussion.

XRD results showed that the peaks of the Ni_2P phase were shifted to a lower Bragg angle, indicating an expansion of the crystal structure due to the insertion of Mo in the structure and the reference sample MoP/SiO_2 did not show any diffraction peak. These results suggested the formation of bimetallic Ni-Mo phosphides NPs. HRTEM analyses confirm the expansion of the cell parameters, and the formation of spheric nanoparticles with a narrow distribution which is maintained after the incorporation in the support. The particle size in the MoP/SiO_2 sample was clearly lower (2.6 nm) with respect to the other NPs samples (9-13 nm). The catalytic activity in the HDO of methyl laurate of the samples with high contents of nickel (Ni_2P and $Ni_{1.6}Mo_{0.4}P$) was low, whereas MoP and Ni_1Mo_1P were very active catalysts (Figure 1). This trend was similar in both temperatures and liquid space velocity studied. The selectivity of hydrocarbons changed with the ratio Mo/Ni in the catalyst, the main hydrocarbon products were C11s with Ni_2P sample, increasing the proportion of C12s with the amount of Mo. This fact, clearly indicates that Ni_2P favors the decarbonylation/decarboxylation pathway while MoP species favored the hydrogenation path. In all cases, the most active catalyst is the reference MoP/SiO_2. The activity of Ni_1Mo_1P was higher than expected for its dispersion in comparison with the reference sample. An analysis of the TOF clearly indicates that the Ni_1Mo_1P presented higher intrinsic activity that points out synergy for the bimetallic catalyst in this reaction.

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Figure SEQ Figure * ARABIC 1. Catalytic activity for hydrodeoxygenation of methyl laurate.

Acknowledgments

The Agencia Estatal de Investigación (AEI) (Spain) supported this work through the project: ENE2016-74889-C4-3-R. DGP acknowledges her contract (BES-2017-079679) to AEI (Spain).

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Nickel alumina-based catalyst for sorption enhanced reforming: Effect of calcination temperature

Lj. Gavrilović[1*], S. S. Kazi[1], A. Oliveira[1], J. Meyer[1]

[1]*Institute for Energy Technology, Kjeller, Norway*
[*]*ljubisa.gavrilovic@ife.no*

Keywords: Ni catalyst, reforming, hydrogen

Introduction. The aim of the present paper is to develop a novel reforming catalyst tailored for Sorption-enhanced reforming process while withstanding multiple reforming-regeneration cycles to provide high H_2 yield and increased catalyst stability. This can be achieved by synthesizing a new Ni catalytic material with improved chemical and mechanical properties by formation of $NiAl_2O_4$ during catalyst calcination after synthesis [1] [2].

Experimental/methodology. A 15% Ni based catalysts was synthesized by the incipient wetness impregnation (IWI) method. The impregnated catalysts were dried and calcined at a different temperature (350°C-850°C) in presence of air (heating rate, 5 °C/min). The synthesized catalyst were characterized by XRD, BET, H2 chemisrotpion, TPR, TGA and SEM. Finally, their catalytic activity was evaluated in packed bed reactor-PBR, under relevant SMR process. The commercial type reforming catalyst was used as a reference for comparison to the in-house synthesized catalyst.

Results and discussion. The samples calcined at higher temperatures (750 and 850 °C) show shifting of the Al_2O_3 peak to a lower angle which indicates the formation of $NiAl_2O_4$[1], confirmed by XRD. The NiO crystallite size was impossible to detect for those calcined above 750 °C due to the formation of $NiAl_2O_4$. TPR results shows that reduction peaks are shifted towards higher temperatures for the catalysts calcined at higher temperature. This indicates that increasing calcination temperature enhances metal-support (Ni-Al_2O_3) interaction and leads to the formation of desired $NiAl_2O_4$ phase. The Ni dispersion decreases when increasing the calcination temperature due to the possible sintering of the Ni particles at higher temperatures. The activity of the two catalysts: commercial type and in-house synthesised, 15Ni/Puralox is presented in Figure 1. It can be seen that SER kinetics of commercial type is slower compared to in-house synthesised one after 100 cycles; this is due to some loss in catalytic activity of the commercial type of catalyst during SER cycles. The in-house synthesised catalyst shows much less deactivation due to the formation of $NiAl_2O_4$. Moreover, the in-house synthesised catalyst showed better resistant towards coking and sintering.

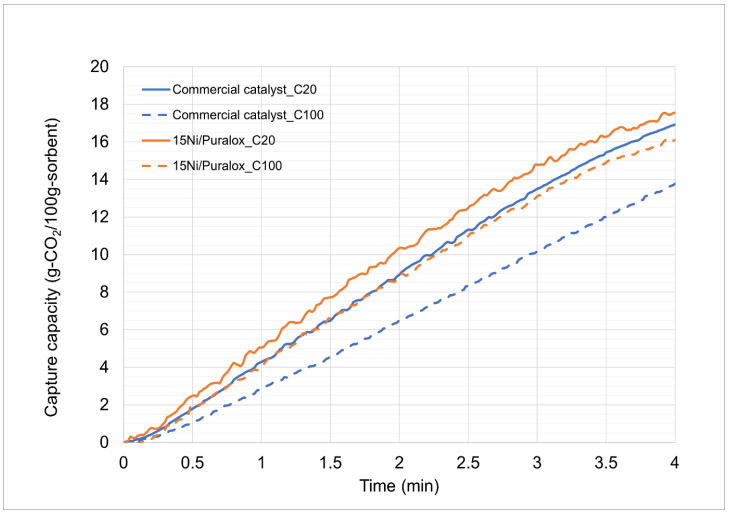

Figure 1. Comparison of catalytic activity of the commercial and 15%Ni/Puralox catalyst in SER TGA. multi-cycles

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Recipe for Highly Dispersed Supported Multi-Metal Catalysts: Towards a Simple, Reliable, Cost-Efficient, and Adaptable Synthesis Protocol

N. S. Genz[1], M. Monai[1], F. Meirer[1], B. M. Weckhuysen[1*]

[1]*Utrecht University, Inorganic Chemistry and Catalysis, Utrecht, The Netherlands*
[*]*b.m.weckhuysen@uu.nl*

Introduction. Supported metal nanoparticles constitute important heterogeneous catalysts and it is well-known that the synthesis crucially determines the resulting, *inter alia*, structure, dispersion, and catalytic performance. Depending on support material, metal(oxide) nanoparticles, and the reaction of interest various synthesis approaches are reported.[1] While for monometallic catalysts syntheses yielding uniform and highly dispersed nanoparticles are reported, general guidelines for multi-metal catalyst systems are scarce. However, systems such as Ni- and Cu-based catalysts are excellent candidates for, e.g., CO_2 methanation and methanol synthesis from CO_2,[2] that is, thermocatalytic CO_2 valorization, which constitutes a promising approach for tackling the problem of continuously increasing global CO_2 emissions and related climate change. For converting CO_2 into other value-added products, Ni-based multi-metal catalysts are promising.[3] Hence, we chose the thermocatalytic CO_2 hydrogenation as showcase for the search of simple, reliable, cost-efficient, and adaptable synthesis protocols yielding highly dispersed metal nanoparticles in multi-metal catalysts. Importantly, this synthesis is easily adaptable, being essential in taking steps towards a more rational design of improved catalyst formulations and our journey towards a more circular society.

Experimental/methodology. Multi-metal solid catalysts were synthesized by an optimized incipient wetness co-impregnation technique. Citric acid (CA) and ethylene glycol (EG) were added to the aqueous nitrate precursor solution. Calcination was performed after the impregnated SiO_2 support was dried for 12 . Advanced characterization by operando infrared (IR) and X-ray absorption spectroscopy (XAS), and high-resolution transmission electron microscopy yielded new insights into the role of CA and EG additives.

Results and discussion. We successfully synthesized a set of small (< 2 nm) and highly dispersed transition metal nanoparticles (consisting of Ni, Fe, and Cu) without metal segregation in mono-, bi-, and trimetallic catalysts. The addition of CA as chelating agent induced an encapsulation of the central metal atoms by the citrate ligands, resulting in smaller and higher dispersed nanoparticles after the ligand removal during calcination.[4] Additionally, adding EG to the precursor solution resulted in enhanced interactions with the support surface, and finally, in smaller and higher dispersed nanoparticles. Importantly, this optimized synthesis was highly reproducible for mono- and multi-metal catalysts with varying metal ratio, demonstrating the great potential for a general guideline for transition metal catalysts. While the removal of EG yielded a minor but significant decrease in CO_2 conversion, that of EG and CA induced a drop in the CO_2 conversion by 25%, showing the importance of both additives.

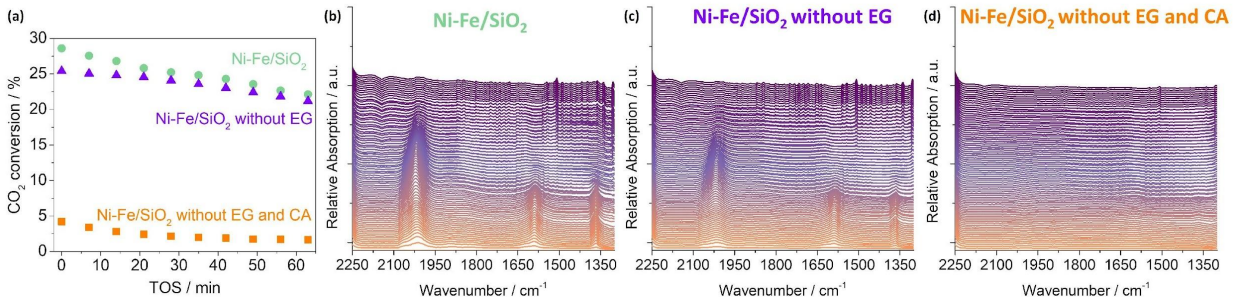

Fig.: Synthesis-dependent conversion during CO_2 hydrogenation at 400°C (H_2/CO_2=4, 1 bar, a) and operando IR spectra (H_2/CO_2=4, 1 bar, 100-400°C, b-d), demonstrating the effect of the addition of citric acid (CA) and ethylene glycol (EG).

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Nickel acetylacetonate on mesoporous zirconia by atomic layer deposition: Initial results

C. Gonsalves[1*], J. Yim[1], A. Chahal[1], E. Haimi[1], M. Mäntymäki[2], J. Velasco[1], R. Karinen[1] and R. L. Puurunen[1]

[1] *Aalto University, Department of Chemical and Metallurgical Engineering, Kemistintie 1, 02150 Espoo, Finland*

[2] *University of Helsinki, Department of Chemistry, P.O. Box 55, 00014 Helsinki, Finland*

**christine.gonsalves@aalto.fi*

Keywords: Atomic layer deposition, heterogenous catalysis, nickel acetylacetonate

Atomic layer deposition (ALD) is a powerful technique for making supported heterogenous catalysts. Due to its self-terminating nature, ALD can produce controlled and uniform metal contents down to single-atom catalysts [1,2]. While ALD has been gaining popularity in the catalysis community [2,3], the first reports of using it to prepare heterogenous catalysts date to early 1990s under the name atomic layer epitaxy and even 1970s under the name molecular layering [4]. Nickel is a known hydrogenation catalyst and owing to its versatility and abundance has also been used industrially in multiple other processes such as biomass gasification and CO_2 methanation [5,6].

This work reports an initial effort to obtain a uniform coating of nickel on mesoporous monoclinic zirconia (m-ZrO_2) using a fixed bed flow type ALD reactor. In an earlier work, it was shown that Ni catalysts can be supported on Al_2O_3 by ALD with Nickel(II) bis(acetylacetonate) as the ALD reactant [7]. Here, we used $Ni(acac)_2$ as the ALD precursor and m-ZrO_2 as the support. Thermogravimetric analysis (TGA) of the reactant $Ni(acac)_2$ confirmed its volatility and stability up to 300 °C. BET surface area of the m-ZrO2 was 60 m^2g^{-1} and the mean pore size was 17 nm. The sample was prepared by calcination of the m-ZrO_2 at 600 °C in air after which it was loaded in a fixed bed ALD reactor. $Ni(acac)_2$ was vaporized at 165 °C (varied from 155 to 180°C) and carried by N_2 to the support. ALD reaction temperatures were varied from 200 to 240 °C. Also, the effect of the reactant exposure time on nickel loading was studied by changing the exposure duration between 120 min to 240 min. Ni loading on the ZrO_2 support was studied by X-ray fluorescence spectroscopy and inductively coupled plasma optical emission spectroscopy (ICP-OES). Acetylacetonate (acac) ligand removal was observed at 550 °C by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) combined with mass spectrometry (MS). The distribution of nickel within a m-ZrO_2 particle was analyzed by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS).

Ni loading increased with increasing reactant dose time from 120 to 240 min and with an increasing ALD reaction temperature from 200 to 240 °C. Nickel distribution by SEM-EDS within a m-ZrO_2 particle was seen although uniformity was not yet observed.

This initial study shows that $Ni(acac)_2$ is a promising ALD reactant to support Ni on mesoporous ZrO_2.

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Two-dimensional (2D) cyanide-bridged heterobimetallic complexes as catalysts for CO_2/propylene oxide copolymerization

G. Penche[1], M. P. González-Marco[1*], J. R. González-Velasco[1], C. M. Kozak[2], C. Vos[2].

[1]*Department of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), Campus of Leioa, P.O. Boz 644, E-48080, Bilbao, Bizkaia, Spain.*
[2]*Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7.*
[*]*mp.gonzalezmarcos@ehu.eus*

Keywords: Environmental catalysis, layered materials, double metal cyanide complexes, CO_2-utilization, copolymerization, epoxide.

Introduction. Square-planar tetracyanonickelate(II) anion ($[Ni(CN)_4]^{2-}$) has historically been used as a design element in the synthesis of cyano-bridged two-dimensional (2D) coordination compounds, including the well-known Hofmann-type clathrates and their analogues [1]. 2D structures are of considerable interest in catalysis because of their high surface-to-volume ratio and ease of access to the active sites. Thus, in this work, we report the synthesis, characterization and catalytic performance in the ring-opening copolymerization (ROCOP) of CO_2 and propylene oxide (PO), a green route to obtain biodegradable and biocompatible polypropylene carbonate (PPC) [2], of four 2D cyanide-bridged bimetallic complexes based on the tetracyanonickeltate(II) building block ($T[Ni(CN)_4]$; T= Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}).

Experimental/methodology. The complexes were prepared by a *tert*-butanol (TBA)-assisted coprecipitation method. Their physico-chemical properties were thoroughly characterized by FT-IR, Raman, XRD, HT-XRD, TGA-MS, SEM, TEM, N_2 physisorption, NH_3-TPD, elemental analysis, and WDXRF. Catalytic activity tests were carried out in a 300 mL autoclave reactor using 2500 ppm of catalyst (vs PO), 20 bar pressure of CO_2, at 90 ºC and 120 ºC and over a 24 h run. A 100 mL Parr reactor equipped with a bottom-mounted Si-comp ATR probe was used for *in-situ* IR spectroscopy studies. Reaction products were characterized by ^{1}H-NMR and GPC.

Results and discussion. Spectroscopic techniques confirmed the bimetallic nature of the synthesized complexes. TEM and SEM microscopy images corroborated their plate-like morphology. The topology and microstructure demonstrated to be dominated by the T atom ability to attract electrons. All complexes were active in the CO_2/PO ROCOP to produce PPCs with low-to-medium CO_2 content (F_{Cu}=13.1-42.4 mol%), medium-to-high molecular weight, (M_n=11000-36500 g mol^{-1}) and high dispersity values (Đ= 2.5-5.0). Undesired propylene carbonate (PC) was formed in all cases (W_{PC}= 0.2-75.9 wt%). Due to its high activity and remarkable selectivity, the kinetics and mechanism of the $Co[Ni(CN)_4]$ complex were further evaluated by *in-situ* IR spectroscopy. A rate law was proposed and determined from the initial rates (**Figure 1**).

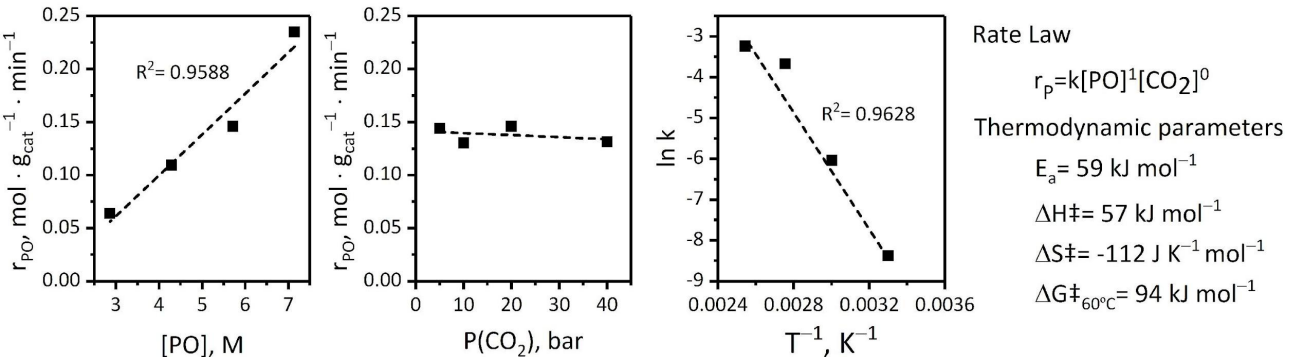

Figure 1. Kinetic study and thermodynamic parameters of the $Co[Ni(CN)_4]$ catalyzed CO_2/PO ROCOP.

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Single-atom catalysts: Recent developments for the CO_2 and CO hydrogenation reaction

A.I. Latsiou[1], N.D. Charisiou[1], A.I. Tsiotsias[1], Z. Frontistis[1], M.A. Goula[1*]

[1]*Department of Chemical Engineering, University of Western Macedonia, GR-50100, Greece*
[*]*mgoula@uowm.gr*

Keywords: CO_2 hydrogenation, higher alcohols, single atom catalysts, C-C coupling reaction

Abstract

The ever-increasing population of the world and the improvement in living standards necessitates the production of more and more energy, which in the majority is still met by the combustion of finite fossil fuels. This in turn leads to an increase in the CO_2 concentration in the atmosphere, one of the main greenhouse gases, intensifing, thus, the phenomenon of global climate chanage.[1] A promising pathway to mitigate CO_2 emissions and its impact on the environment is by its catalytic transformation to fuels and other chemicals, such as CO, CH_4, CH_3OH, $C_{2+}H$ and $C_{2+}OH$. Carbon dioxide hydrogenation constitutes a promising reaction which can proceed via thermal-, photo- or electro- catalysis.[2] Among the aforementioned products, the investigation of the synthesis of higher alcohols (HAs), important chemicals in the fuel sector, is still at an early stage, in comparison with the other platform chemicals. This can be attributed to the difficulty of the reaction mechanism, as HAs consist of one C-O bond and at least one C-C bond and the success of C-C bond formation poses a formidable challenge.

Today the catalysts that are used the most in τηε industry are the conventional supported heterogeneous catalysts consisting of nanoparticles or clusters of the active metal dispersed on the surface of the support. However, these catalysts have two major limitations; firstly, their selectivity is low as only a part of the active sites participates in the reaction, and secondly the amount of noble metal needed is relatively high.[3] Therefore, in an effort to overcome these disadvantages researchers now turn their attention to reducing the size of the active phase to single atoms in order to increase catalytic performance and lower costs.

Single atom catalysts (SACs) have in the last decade emerged as a new class of materials combining the advantages of homogeneous and heterogeneous catalysts, i.e., well-defined sites, easy separation, high catalytic activity, selectivity and stability.[4] However, the most important feature of this kind of materials is that they contain only isolated metal atoms achieving, thus, a 100% atom utilization. Therefore, these catalytic materials provide the maximum possible metal dispersion taking full advantage of the metal active sites and minimizing the noble metal content needed. Until now, numerous SACs proved to have an outstanding catalytic performance in a variety of reactions such as CO oxidation, water-gas shift, selective hydrogenation, CO_2 reduction and C-C coupling.

For this reason, research regarding the CO_2 hydrogenation reaction has lately been focused on the development and investigation of new and innovative single atom catalysts for the enhancement of product yield. Thus, this review focuses on the recent advances in the use of single-atom catalysts for the thermo-, photo-, and electro- chemical hydrogenation of CO_2 and CO for the synthesis of a variety of chemicals (methanol, carbon monoxide, formic acid, higher alcohols) through the presentation, comparison and critical discusion of the different catalytic systems that have been used so far.

Acknowledgments

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Studies on potassium-promoted cobalt catalysts for ethanol steam reforming

M. Greluk[1*], M. Rotko[1], G. Słowik[1], G. Grzybek[2], A. Kotarba[2]

[12]*Faculty of Chemistry, Maria Curie-Sklodowska University in Lublin, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland*

[1]*Faculty of Chemistry, Gronostajowa 2, 30-387 Krakow, Jagiellonian University, Poland*

[*]*magdalena.greluk@mail.umcs.pl*

Keywords: cobalt catalysts, alkali doping, hydrogen production, ethanol steam reforming

Introduction. Hydrogen energy has received considerable attention due to its high specific energy density and environmental benefits. Among a variety of strategies for hydrogen production, ethanol steam reforming (ESR) is a promising route because CO_2 yielded during this reaction could be reused through the photosynthesis of plants, which can be used as feedstock for ethanol production by fermentation, thus forming a closed carbon loop cycle. Catalysts for ESR should have the ability to break the C–C bond. Noble metal catalysts, such as Rh, Ru, Pt, and Pd, are excellent catalysts for C–C bond cleavage. However, due to their high price, transition metal (Ni or Co) catalysts are frequently used for the ESR process. Their performance in the ESR process can be additionally enhanced by alkali promoters' application. Reportedly, the addition of alkali promoters to Co or Ni-based catalysts is effective for promoting ESR reaction and suppressing carbon deposition [1-4].

Experimental/methodology. The Co/CeO_2 catalyst with nominal metal loading of 10 wt% was prepared by wet impregnation of the commercial nano-dispersed ceria support (Aldrich, particle size: <25 nm particle size, DP:14 nm, VP: 0.14 mL/g, S_{BET}: 42.5 m^2/g) with the solution of $(CH_3COO)_2Co \times 4H_2O$ in ammonia solution, 25%. KCo/CeO_2 catalysts with nominal potassium loading of 0.5 and 1.4 wt% were prepared by wet impregnation method of finely grinded Co/CeO_2 solid with solutions containing KNO_3. Complementary characterization techniques, such as XRD, XRF, low-temperature nitrogen adsorption, SEM, TEM, and H_2-TPR, were used to correlate surface structure and functionality with the catalytic performance of catalysts. The ESR reaction for $EtOH/H_2O$ molar ratios of 1/4 and 1/12 and at temperatures from 420 to 540 °C was carried out over the pre-reduced (T = 500°C, p = 1atm) samples in the flow reactor.

Results and discussion. For $EtOH/H_2O$ molar ratio of 1/4, a temperature of 540 °C was sufficient to obtain complete ethanol conversion during 21 h of the ESR process with very high selectivity to hydrogen (92%) and carbon dioxide (60%) and only two by-products, methane and carbon monoxide, over $1.4KCo/CeO_2$ catalyst. In the case of the Co/CeO_2 sample, this temperature allowed obtaining the ethanol conversion of 90% after 21 hours of the ESR process. Moreover, C2 by-products, acetaldehyde and ethylene, were formed in the presence of this catalyst. Potassium doping of the Co/CeO_2 catalyst allowed not only to enhance steam reforming activity but also to suppress the aldol condensation of acetaldehyde to acetone. In addition, potassium doping inhibited the accumulation of carbon on the catalyst surface under the ESR conditions favoring the rate of the steam gasification of carbon formed during the process. Although the potassium addition did not influence the morphology of formed carbon, it seems to depend on the temperature of the ESR reaction. For 420 °C on the catalysts' surface mainly the polymeric carbon encapsulating the cobalt particles was formed, resulting in the immediate deactivation of Co/CeO_2 catalysts. Whereas the filamentous carbon, resulting from the methane decomposition and carbon monoxide disproportion reactions, was mostly formed during the ESR reaction carried out at 540 °C.

Acknowledgements

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Pd-Pt nanoparticles supported on CeO_2 nanorods and nanocubes for emission control

Andrea De Giacinto[1,2], Paolo Dolcet[2], Maria Casapu[2], Jan-Dierk Grunwaldt[2], Silvia Gross[1,2*]

[1] *Dipartimento di Scienze Chimiche (DiSC), Universita` degli Studi di Padova (UniPD), via Marzolo, 1, 35131, Padova, Italy*

[2] *Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Engesserstraße 20, 76131 Karlsruhe, Germany*

[*]*Corresponding Author's E-mail address silvia.gross@unipd.it*

Introduction.

Air pollution is a major problem all over the world, affecting human health, ecosystems, and climate change. The transport industry has been recognised by the European Environment Agency as one of the first sources of air pollution in Europe[1]. The field of automotive catalysts is always under development, also to comply with more stringent emission regulations. In this framework, a fundamental understanding of the reactions occurring in a catalytic converter can help to reduce the amount of noble metals employed. The interest toward cerium oxide-based materials as supports for catalytically active nanoparticles has raised in the last decades due to oxygen storage properties of ceria[2], and it has recently been shown that using CeO_2 as supporting material instead of the conventional Al_2O_3 can significantly improve the activity for CO oxidation[3]. CeO_2 represents an example where fundamental studies can help in better understanding the contribution of active support materials, since morphological features can be tuned during its synthesis, with the aim to modify surface properties, influencing the catalytic performances[4].

Experimental/methodology.

The present work concerns the synthesis of well-defined anisotropically shaped CeO_2 nanostructures. Homogeneous and well-defined CeO_2 nanorods and nanocubes were successfully obtained through subcritical hydrothermal synthesis and consequently impregnated with small ($d < 5$ nm) and monodisperse PdPt bimetallic nanoparticles (NPs) produced *via* chemical reduction in a microfluidic reactor. A commercial CeO_2 with no preferentially exposed facets was used as a benchmark.

Results and discussion.

Through different analytical tools crystal structure (XRD), morphology and exposed facets (SEM, HRTEM), specific surface area and porosity (N_2 physisorption), noble metal loading (ICP-OES), and reducibility (TG-MS), have been determined. The catalysts were also tested for CO oxidation in a model gas mixture, under constant weight hour space velocity (WHSV), to reveal the effect of different exposed facets of the support in the catalytic performance. O*perando* XAS data were additionally acquired on Pd and Pt edges at ESRF. The catalytic activity data show clear differences between the performance of the bimetallic Pt-Pd catalysts supported on different anisotropically shaped CeO_2, which could be releted to their properties and redox behaviour.

Acknowledgments.

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Influence of deposition method on activity of Ru@magnetic C catalysts on hydrogenation of hydroxymethyl furfural to 2,5-Bis(hydroxymethyl)furan

S. Gyergyek[1*], A. Murovec[1,2], Ž. Ponikvar[1,2], J. Teržan[3], M. Grilc[3], B. Pomeroy[2,3], B. Likozar[3], D. Makovec[1]

[1] *Department for Synthesis of Materials, Jožef Stefan Institute, Ljubljana, Slovenia*
[2] *Facutly of Chemistry and Chemical Engineering University of Maribor, Maribor, Slovenia*
[3] *Department of Catalysis and Reaction Engineering, National Institute of Chemistry, Ljubljana, Slovenia*
[*] *saso.gyergyek@ijs.si*

Keywords: Ruthenium, magnetic catalyst, hydrogenation, hydroxymethylfurfural

Introduction. 5-hydroxymethylfurfural (produced from lignocellulosic biomass) shows immense potential for forming a vast range of platform chemicals for bio-polymers and biofuel production [1]. Therefore, selective and active catalysts for its transformation are critical for its utilization. Here we show that the choice of preparation method for deposition of a well known and active catalysts for hydrotreatments of biobased chemicals i.e., Ru [2] can have a profound effect on its activity and selectivity.

Experimental/methodology. A series of catalysts was prepared on a magnetic C support by a two-step procedure. In the first step of preparation the magnetic C support was prepared [3]. In the second step Ru was deposited: by impregnation, followed by drying and reduction in H_2 atmosphere at 250 °C. (Catalyst I); precipitation of Ru^{3+} in presence of magnetic C, followed by drying (P) and reduction in H_2 atmosphere at 250 °C (PR) and by a solvothermal reduction of Ru^{3+} by isopropanol in presence of magnetic C (ST). Prepared and spent catalysts were characterized and analyzed in great details by conventional methods. Catalytic hydrogenations of 5-hydroxymethylfurfural (HMF) were carried at 130, 150 and 170 °C at 5 MPa of H_2. Reaction rate constants and activation energies were determined by microkinetic modeling [4].

Results and discussion. TEM and STEM analysis showed that impregnation method followed by reduction of $RuCl_3$ to metallic Ru nanoparticles yielded the least homogenous dispersion of Ru over the surface of magnetic carbon. Such poor homogeneity of distribution can be associated to uneven deposition of $RuCl_3$ from aqueous solution in the impregnation step. The magnetic support is porous and therefore uneven drying and consequently uneven deposition is expected. Upon reduction the average size of Ru nanoparticles was 1.5 ± 0.3 nm. Solvothermal reduction of $Ru(acac)_3$ yielded relatively homogenous distribution of Ru nanoparticles of 1.7 ± 0.3 nm in diameter however, larger Ru platelets of 5 to 10 nm in size were frequently observed as well. Precipitation of Ru^{3+} in presence of magnetic carbon results in homogeneous deposition of small approx. 1 nm sized Ru oxide/hydroxide nanoparticles. Those reduce to 1.3 ± 0.3 nm sized Ru nanoparticles when used for hydrogenation of HMF already at 130 °C. However, when reduced in H_2 in tubular furnace at 250 °C they grow to 3.2 ± 0.3 nm sized Ru nanoparticles. XRF determined content of Ru was comparable, approx. 4 wt.% for all of catalysts except for ST where 2.6 wt.% was determined. Their activity for HMF hydrogenation was markedly different. The PR catalysts showed the worst performance that could be related to the largest size of Ru nanoparticles found in that catalyst. The best performance in terms of activity, selectivity and stability was demonstrated by P catalyst. We attribute such behavior to the unique conditions of its reduction being conducted under reactive conditions.

Acknowledgments

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Efficient Catalysts for Methylcyclohexane Dehydrogenation: Dispersed Cluster Fe Decoration of SiO_2 Supported Pt Catalysts

H. Akhoundzadeh[1], R. Xu[*]

[1]*Nanyang Technological University, Singapore, Singapore*
[2]*Nanyang Technological University, Singapore, Singapore*
[*] *rxu@ntu.edu.sg*

Introduction.

Liquid organic hydrogen carriers (LOHCs) hold tremendous promise for hydrogen storage and transportation, with methylcyclohexane (MCH) being among the most favorable candidates. However, the dehydrogenation of MCH presents a significant challenge due to the lack of efficient catalysts. Traditionally, platinum (Pt) catalysts have been utilized for MCH dehydrogenation, but they suffer from rapid deactivation and low selectivity. The main objective of this study is to enhance the performance of Pt catalysts by incorporating Fe as a promoter while carefully controlling the size of Fe particles. To achieve this goal, we synthesized two different sizes of Fe particles and subsequently added Pt to the catalysts.

Experimental/methodology.

To synthesize SiO_2-supported Pt-Fe bimetallic catalysts, Fe-citric acid and $Fe(NO_3)_3$ were used as Fe precursors for which the resulting samples were designated as Fe/SiO_2-S (S for small Fe particles) and Fe/SiO_2-B (B for big Fe particles). Subsequently, $Pt(NH_3)_2(NO_3)$ was loaded.

Results and discussion.

In order to investigate the effect of Fe particle size and bimetallic formation, transmission electron microscopy (TEM) was used. As can be seen from Fig.1a and b, Fe particle size was around 1 nm in Fe/SiO_2-S sample while Fe size was much larger than F/SiO_2-B sample(4nm). Fig1. shows the lattice fringe of PtFe samples is 0.21 nm which is lower than Pt(111) which is 0.23 nm, confirming Pt-Fe alloy formation.

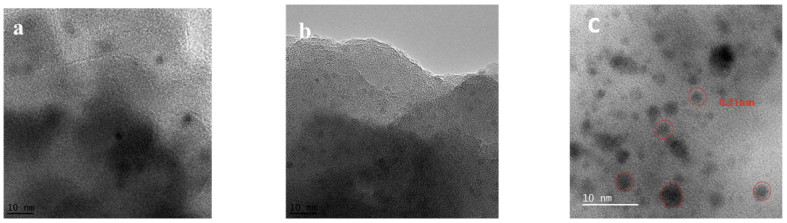

Fig1. TEM images of different supported Fe samples; a) Fe/SiO_2-B, b) Fe/SiO_2-S and $Pt\text{-}Fe/SiO_2$-S.

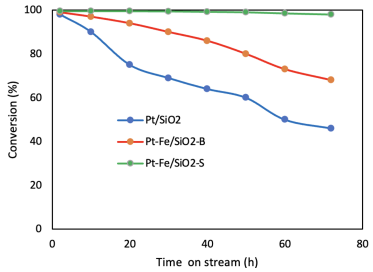

Fig 2. the catalytic performaance of different catalysts in MCH dehdyrogenation.

Fig. 2 illustrates the catalytic performance in MCH dehydrogenation, clearly indicating that the non-modified Pt/SiO_2 catalyst deactivated rapidly. However, with the addition of Fe, the performance improved, though to varying degrees depending on the size of the Fe particles. Notably, $Pt\text{-}Fe/SiO_2$-S exhibited significantly more stable performance than $Pt\text{-}Fe/SiO_2$-B, underscoring the critical role of promoter particle size. Smaller Fe particles provide a higher number of particles that can strongly interact with Pt. Remarkably, the $Pt\text{-}Fe/SiO_2$-B catalyst displayed an impressive hydrogen evolution rate of 2200 $mmol.gPt^{-1}.min^{-1}$, and even after 3 days, the conversion remained at around 98%. This research introduces a

pioneering technique for producing supported Pt-Fe catalysts, with a primary focus on precise control over the dimensions of Fe particles as a promoter.

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Evaluating the effect of fiberous ZrO_2 support the catalytic performance of a hieriachical Ni catalyst in DRM

M. Halabi[1], O. Naseraldeen[1], L. Giloni[1], M. Lahav[1], G. Grader[1] and O. Gazit[1*]

[1] *Faculty of Chemical Engineering, Technion, Israel Institute of Technology, Haifa 3200003, Israel* [2]*Second*
[*] *ozg@technion.ac.il (O.M. Gazit)*

Introduction

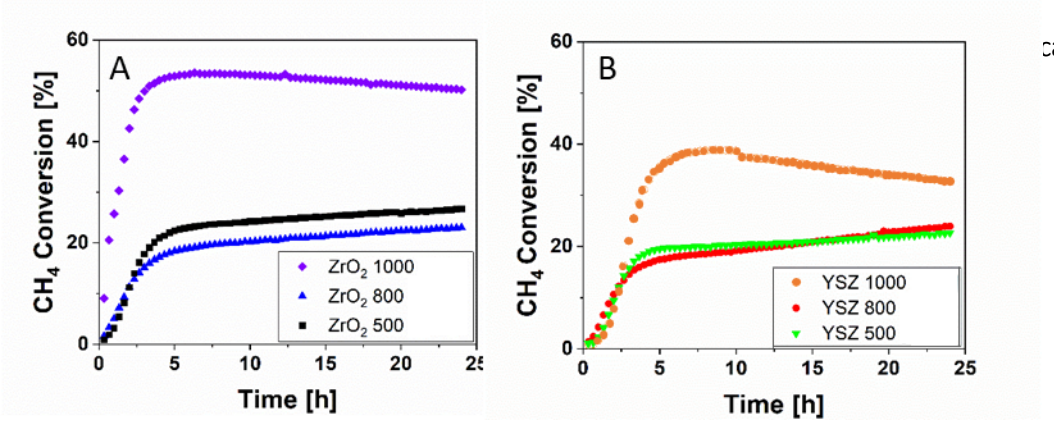
Methane dry reforming is a well-studied reaction that have both scientific and industrial importance. It has gained much attention in recent years for its ability to convert two greenhouse gasses, CH_4 and CO_2, into syngas to produce a wide range of products.[1] The best-known catalysts for DRM are based on noble metals, which are not viable for an industrial process due to their high cost. This can be overcome by using transition-metal based catalysts such as nickel (Ni). However, Ni based catalysts suffer from strong deactivation, which can be caused by carbon deposition on catalyst's surface, sintering of the Ni particles and blockage of the catalyst support pores. Recent work within the Gazit group showed that a Ni catalyst supported on a hierarchical support, composed of a thin mixed metal oxide supported on a secondary underlying metal oxide, has great potential for the promotion of DRM reaction.[4] However, the nature and extent of interactions between the Ni and the hierarchical support and how they affect DRM catalysis is still not fully understood. In this work we evaluate the effect of the underlying ZrO_2 support morphology and phase on the hierachical Ni based catlayst catalytic performance.

Experimental/methodology

Nanofibers(NFs) of ZrO_2 and yittrium doped ZrO_2 (YSZ) were electrospun. The morphology of the NFs was characterized by high resolution scanning electron microscopy (HR-SEM), Temperature programed reduction experiments (TPR), powder X-ray diffracion (XRD) and ICP-OES. Catalytic activity was evaluated at 800 °C and atmospheric pressure in a fixed-bed quartz tubular reactor. The products were analyzed using an online GC.

Results and discussion

To induce morphological changes, the ZrO_2 YSZ NFs were calcined at different temperatures perior to hierarchical catalyst preparation. Using those materials as the underlying support for Ni we prepared 6 different catlayst and tested those in DRM. It was found that supporting the Ni on the hierarchical NFs calcined at 1000 °C produced a catalyst with the highest CH_4 conversion and H_2/CO ratio, Figure 1. comparing these resutls to structural parameter obtained by XRD we identify chnages in crystalline phase and in grain size. Furthermore, comparing the results to particular ZrO2 we find that the NFs geometry gives advantageous performance.



calcined at different

B-site Ni doping in double perovskite enhancing electrochemical catalytic properties

K. Han[1], J. Song[1], Y. Jeon[1*]

[1]*Department of Environmental and Energy Engineering, Yonsei University, Wonju, Republic of Korea*

[*]*Corresponding Author's E-mail address: [*]ykjeon@yonsei.ac.kr*

Keywords: Double perovskite, Electrocatalyst, Oxygen Evolution Reaction

Introduction.

The use of perovskite materials has been steadily increasing from the past to the present, and research is being conducted to find excellent durability and efficiency suitable for each field. [1] The characteristics of perovskite materials include high melting points, high hardness and strength, and considerable durability, but problems include low electrical and thermal conductivity and chemical inertness.[2]

Double perovskite structured material, $A_2BB'O_6$ is used in many electrochemical fields because of its good electrical properties, and its unique structure-property, of layer-by-layer, which is considered to have good structural advantages.

In this work, the electrocatalyst using tungsten (W) based double perovskite was designed. To make the stable structure, calcium (Ca) was used for stabilization, and a transition metal of nickel (Ni) was doped in the structure as an active site for improving electrocatalytic properties.

Experimental/methodology.

$Ba_2Ca_{1-x}Ni_xWO_6$ double perovskite catalysts were synthesized by the solid-state method. The mixed powder was calcinated in an alumina boat in the furnace at 800 ℃ for 24h and 1400 ℃ for 48 h.

Results and discussion

Prepared double perovskite structure catalysts of $Ba_2Ca_{1-x}Ni_xWO_6$ resulting in high crystallinity and good electrochemical properties. Each of the metals is finely positioned in certain rations, which was confirmed by the XRD, SEM & EDX analysis.

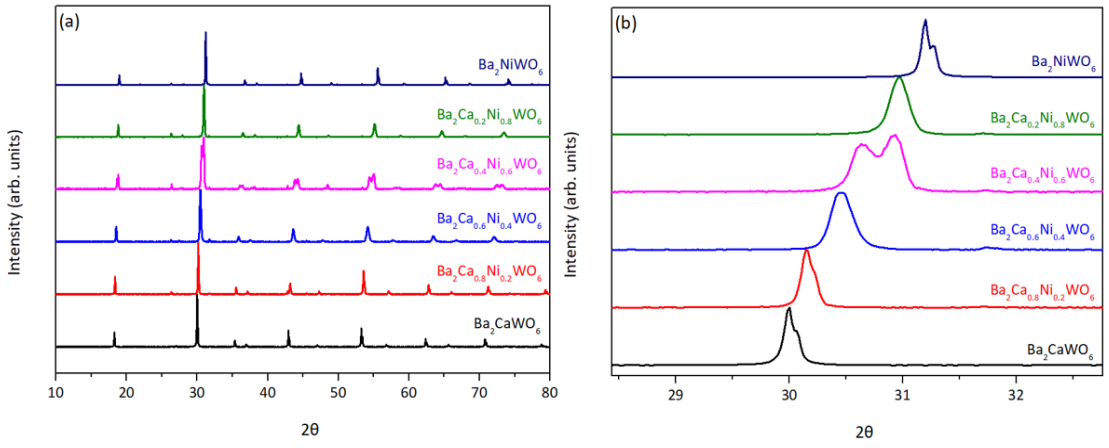


Fig. 1. (a-b) The XRD pattern of $Ba_2Ca_{1-x}Ni_xWO_6$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1) shows the structure change when nickel doping amount becomes larger and the difference between calcium ion size and nickel ion size.

In XPS, there is a structural change when a portion of nickel increases depending on the calcium portion. From the electrochemical results, we can confirm that double perovskites with optimized Ni and Ca ration have great electrical properties, which indicates the importance of the structural design of the electrochemical catalysts.

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Hierarchical Hollow Al-Rich Nano ZSM-5 Crystals for Highly Selective Production of Light Olefins from Naphthene

Lei Han*, Ruoyu Wang, Peng Wang, Wei Lin
Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, China.
han-lei.ripp@sinopec.com

Keywords: Al-rich ZSM-5, hierarchical zeolite, hollow structure, desilication, naphthene cracking

Introduction.

As one important member in crystalline aluminosilicates MFI family, ZSM-5 zeolites possess distinctive small microporous structure (~0.56 nm) and exhibit favorable shape-selectivity for enhanced light olefin yields in industrial catalytic cracking processes and many other fundamental petrochemical processes[1]. However, ZSM-5-catalyzed reactions may encounter with molecule diffusion problems due to limited pore size, leading to unwanted coke deposition and further deactivation, especially in the case of bulky cyclic compounds[2].

Methodology.

We report a facile Al-distribution regulated desilication approach to synthesize hierarchical Al-rich nano ZSM-5 crystals with hollow structures. Briefly, this approach involves (i) the synthesis of parent ZSM-5 zeolites with high percentages of local concentrated Al (Z5-LCA) domains and (ii) post-treatment of Z5-LCA with NaOH solution (Fig.1). The existence of LCA domains and their impacts on the selective desilication process were validated by diffuse reflection UV spectra and filtrate analysis, and approximately 49% of Al atoms emerged in Z5-LCA samples as Al species in close contact.

Results and discussion.

The as-synthesized Z5-LCA is primarily in round pancake shape with uniform sizes of around 600~1000 nm. Distinct hollow ZSM-5 zeolite can be obtained using more concentrated base (0.6 M of NaOH) in the post-treatment procedure. The hollow ZSM-5 zeolite is characteristic of type IV BET isotherm curves, and pronounced H4 hysteresis loops in the relative pressure range of p/p_0 = 0.45~0.85, indicating the generation of mesoporous cavities. Compared with its parent zeolite, the hierarchical hollow nano ZSM-5 crystal exhibited increased catalytic activities as well as ~ 2-fold improved selectivities for high-value light olefins (C_2H_4 and C_3H_6) in the catalytic cracking of decalin (a model bulky naphthene molecule) (Fig.2). These findings expand our knowledge on achieving desirable zeolite structures by regulating framework Al distribution, and suggest a promising new catalyst toward highly selective production of light olefins from naphthene feedstocks.

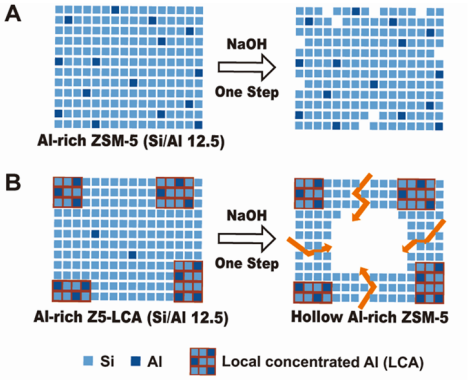

Fig. 1 (A) Schematic illustration of the solid mesoporous ZSM-5 obtained after one-step alkaline treatment of regular Al-zoned ZSM-5 with a low Si/Al molar ratio. **(B)** Hierarchical hollow Al-rich ZSM-5 obtained after one-step alkaline treatment of parent Al-rich ZSM-5 with local concentrated Al atoms (Z5-LCA).

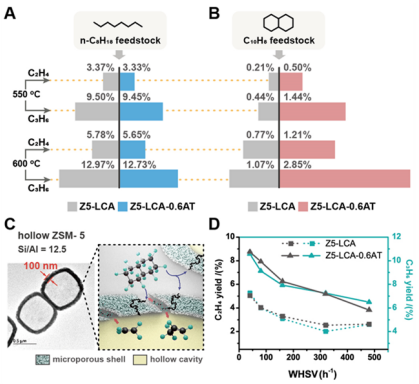

Fig. 2 Light olefin yields in the cracking reactions of **(A)** n-octane and **(B)** decalin catalyzed by parent zeolite (Z5-LCA) and Al-rich hollow ZSM-5 (Z5-LCA-0.6AT). **(C)** Schematic illustration of the improved diffusion properties of Z5-LCA-0.6AT. **(D)** Light olefin yields in the cracking reactions of naphtha feedstocks catalyzed by Z5-LCA and Z5-LCA-0.6AT under different WHSV conditions (600 °C).

Acknowledgments

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Effects of Silica and Barium Oxide Addition to Alumina Carriers for Steam Reforming

A. Hasegawa[1], S. Ogasawara[2], H. Nakamura[2], K. Matsuda[2], Y. Kadoma[1], M. Kobune[1], T. Honma[1], T. Nonouchi[2], O. Okada[2]

[1] *National Institute of Technology (KOSEN), Hachinohe College, Hachinohe, Japan*
[2] *Renaissance Energy Research Co., Ltd., Osaka, Japan*
[*] *hase-c@hachinohe-ct.ac.jp*

Keywords: Alumina carrier, Heat resistance, Coking, Steam reforming

Introduction.

Catalysts for steam reforming reactions must maintain a high specific surface area in a steam atmosphere at high temperature and high pressure, and must also suppress coking. We have reported that silica-doped alumina prepared by coprecipitation exhibits extremely high heat resistance. However, the addition of silica tends to induce coking [1]. Therefore, in the present study, silica and barium oxide were added to alumina to prepare an alumina carrier with both heat resistance and coking resistance.

Experimental.

Ethyl silicate was added to the aluminum nitrate solution and stirred to obtain a homogeneous solution. Ammonia water was then added to this solution to form a precipitate. After filtration and washing of the precipitate, an aqueous barium nitrate solution was added and evaporated to dryness at 150°C. The dried powder was calcined at 1000-1200°C to obtain the alumina carrier. Nickel-supported catalysts were prepared on the resulting alumina supports by the impregnation method, and the amount of coking was evaluated by a steam reforming reaction using propane.

Results and discussion.

We prepared alumina samples with silica, barium oxide, and lanthanum oxide, and evaluated their heat resistance. The silica-doped alumina exhibited the highest heat resistance [2]. The specific surface area of the alumina carrier increased with increasing silica content, indicating that silica is effective for improving heat resistance [3]. However, the solid acidity of the alumina carrier was evaluated by NH_3–temperature-programmed desorption and was found to increase with increasing silica content. The amount of coking was evaluated by a steam reforming reaction with propane using a Ni-SiO_2/Al_2O_3 catalyst. For catalysts with 3% or more of added silica, the amount of coking increased rapidly with increasing silica content. Therefore, alumina supports were prepared with various amounts of added silica and barium, and the specific surface area and solid acid content were evaluated. As shown in Figure 1, the 7% BaO-1% SiO_2/Al_2O_3 carrier showed a specific surface area of 34 $m^2 \cdot g^{-1}$ after heat treatment at 1200°C for 30 h, while the solid acidity was comparable to that of alumina without silica. These results indicate that BaO-SiO_2/Al_2O_3 exhibits high heat resistance but suppressed solid acidity.

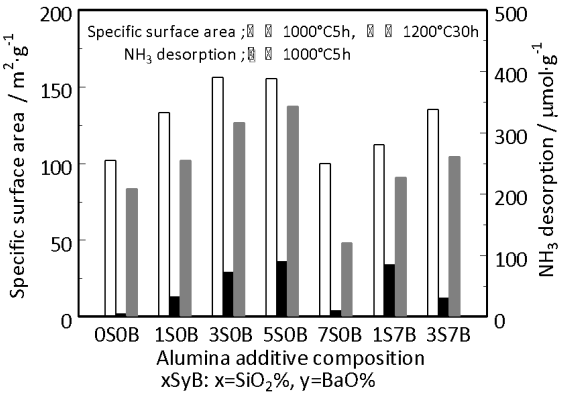

Figure 1. Specific surface area and solid acid content of alumina carriers with various amounts of added silica and barium oxide.

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Carbon Neutral Isobutanol – Development of high performance catalysts based on dilute alloys

J. Häusler[1*], J. Pasel[1], R. Peters[1]

[1]*Forschungszentrum Jülich GmbH, Jülich, Germany*
[*]*j.haeusler@fz-juelich.de*

Keywords: Guerbet Reaction, Carbon Neutral Fuels, d-Band Center, Catalytic Activity, C-Methylation

Introduction. To mitigate CO2 emissions in society, it is imperative that products utilized on a large scale are produced utilizing CO2 sources. The primary contributors to CO2 emissions are fossil fuels, accounting for 18% of the worldwide CO2 emissions in 2019 due to road traffic[1]. Carbon-neutral fuels can reduce the climate impact but to be used in existing consumer cars, they have to match the characteristics of fossil fuels. Methanol can easily be synthesized from CO2 and renewable hydrogen but does not meet these requirements. Because direct usage of methanol or even ethanol in higher concentrations is incompatible and restricted by the DIN EN 228 and ASTM D7862 in cars, the efficient synthesis of C4 alcohols is a central part of the project. These C4 or "higher alcohols" prove to meet preceding regulations and burning characteristics.

Because of this a lot of research nowadays deals with the upgrading of ethanol into 1-butanol through the Guerbet reaction, since 1-butanol has a higher caloric value, is less aggressive and more hydrophobic than ethanol[2,3]. Since 1-butanol has a higher caloric value, is less aggressive, and is more hydrophobic than ethanol[2,3]. A huge disadvantage of this reaction is the low conversion of ethanol and low selectivity towards 1-butanol. Using methanol for the methylation of ethanol and NaOH as a cheap and abundant base allowed the selective synthesis of 2-methyl-1-propanol (iso-butanol)[4,5]. In the context of a CO2-neutral methanol-based fuel synthesis, this is advantageous, as 50% of the carbon atoms are methanol-originated, and by using bio-ethanol a carbon-neutral product can be achieved.

For our research, we decided to build upon this C-methylation protocol for the synthesis of iso-butanol, because i-butanol is not only suitable as a drop-in fuel but also as an educt for octane enhancers and monomer for polymers and thereby offers a product suitable to exchange fossil based iso-butanol[6]. In this study, we aim at understanding the underlying influences of the active metal in the synthesis of i-butanol.

Experimental/methodology. For the search of activity trends in the metals we used monometallic catalysts and correlated their activity against the d-Band center. After identification of the best-performing catalyst based on isobutanol yield, we synthesized bimetallic catalysts with calculated d-Band values near the optimal catalytic metal. Further, the bimetallic catalyst with the highest catalytic activity was chosen for further optimization experiments, by varying metal loading and metal-to-metal ratio.

The catalysts for the reaction were prepared by impregnation and precipitation methods on activated carbon, drying, and where necessary subsequent impregnation with the appropriate amount of platinum precursor. All of the catalysts were characterized through STEM, ICP-OES, H2-Chemisorption, XRD, and N2-Physisorption. Catalytic tests were performed in a Parr batch Autoclave reactor of 70mL Volume. Product analysis and quantification of liquid samples were performed with GCMS.

Results and discussion. For the monometallic catalysts a volcano plot was achieved when the TOF calculated from STEM and chemisorption experiments was correlated with the d-band-center value of the transition metals, Cu (-2,67 eV), Pt (-2,25 eV), Ir (-2,11 eV), Pd (-1,83 eV), Rh (-1,73 eV) and Rh (-1,41 eV). Platinum reached the maximum TOF of 16,25 h-1 while there was a monotonic decrease of TOF for the metals with higher or lower d-band center values. This result led us to the assumption that an optimal adsorbate-adsorbent interaction was reached at the d-band center value of -2,25 eV, following the Sabatier-Principle [7]

Synthesis, characterization, and experimental testing of the highly diluted bimetallic alloys Cu99Ni1/C, Cu99Fe/C, Fe99Pt1/C, Fe99Pd1/C, Ni99Pt1/C resulted in much lower TOFs and did not match the predicted volcano plot when calculating the TOF based on the metal surface area from STEM and XRD measurements. Nevertheless, the Ni99Pt/C catalyst was not deactivated under reaction conditions, while the corresponding Pt/C catalyst deactivated within 1-2 hours depending on the reaction temperature. Optimizing the Ni: Pt

ratio and metal loading, allowed us to reach a 12% yield of i-butanol with a selectivity of 95% after 4h reaction time, while the Pt catalyst only achieved a 2% yield under similar reaction conditions.

Acknowledgments
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Non-Symmetrical Triphos Derivatives and their Application in Ruthenium Catalyzed Hydrogenation Reactions

Johanna Henkel[1], Ole Osterthun[1], and Jürgen Klankermayer[1*]

[1]RWTH Aachen University, Institute of Technical and Macromolecular Chemistry, Aachen, Germany
henkel@itmc.rwth-aachen.de and jklankermayer@itmc.rwth-aachen.de

Introduction. Ruthenium triphos complexes, with [Ru(triphos)(tmm)] (triphos = 1,1,1-tris(diphenylphosphino)ethane; tmm = trimethylenemethane) as the main representative, have been extensively studied for various reactions with a focus on the hydrogenation of carbonates, amides, polyesters, polycarbonates and carbon dioxide (CO_2).[1-3] While mainly [Ru(triphos^{R_3})(tmm)] complexes with the same substituents on the phosphines have been studied in catalytic hydrogenations, little work has been done to understand the effects of triphos systems with altered phosphine arms of the form [Ru(triphos$^{RR'_2}$)(tmm)]. However, this increased complexity allows the tailoring of the ligand environment specifically to the substrate, paving the way to catalytic systems with unprecedented activity and selectivity.
Experimental/methodology. Based on the protocol of Tuczek *et al.*[4], the synthesis of a wide range of triphos ligand derivatives using diisopropylphosphine or dicyclohexylphosphine and two aromatic phosphines is presented here (Figure 1). The corresponding [Ru(triphos$^{RR'_2}$)(tmm)] complexes can be tested for selected hydrogenation reactions.
Results and discussion. The catalytic activity of the synthesized catalysts was tested in the hydrogenation of CO_2 to methanol. For the symmetry broken ligands obtained by introducing electron donating isopropyl groups, an increase of the initial TOF by a factor up to 2 could be observed for all tested catalysts in comparison to the symmetrical [Ru(triphos)(tmm)]. With the introduction of cyclohexyl groups, an increase by a factor up to 2.3 could be achieved. The largest increase in activity could be observed for the ruthenium triphos derivative with one PCy_2 (Cy = cyclohexyl) group and two P(*m*-OMe)$_2$ (*m*-OMe = 3,5-dimethoxyphenyl) groups, resulting in a TOF_{ini} of 327 and a TON for methanol of 1193. We further plan to use the described catalysts for the hydrogenation of selected other substrates.

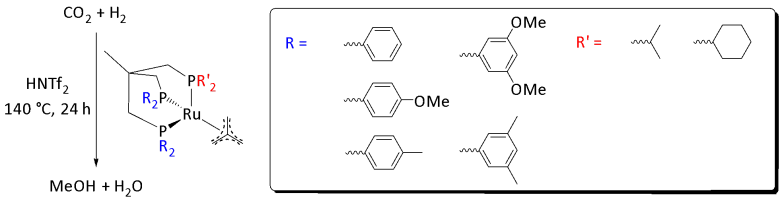

Figure 1: Different [Ru(triphos$^{RR'_2}$)(tmm)] complexes tested in the hydrogenation of CO_2 to methanol.

Classical experimental testing of all candidates for each substrate is impossible due to the expansion of chemical space through symmetry breaking, which leads to a multitude of complex combinations. Therefore, this class of complexes will be studied more closely and explored through the development and application of computational and modern machine learning methods in collaboration with Prof. Bannwarth's group (RWTH Aachen University).

Acknowledgments
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Influence of Support on the Dehydrogenation of Perhydro Benzyltoluene with Platinum-based Catalysts

E. Herzinger[1], M. Wolf[1*]

[1]*Karlsruhe Institute of Technology, Karlsruhe, Germany*
[*]*moritz.wolf@kit.edu*

Keywords: Chemical hydrogen storage, LOHC, dehydrogenation, catalyst preparation, support material

Introduction. Hydrogen as an energy carrier offers many benefits for the environment, energy security, economy and end users.[1] However, cost-effective, compact, safe and convenient storage of hydrogen are essential for large-scale implementation. Further, the volumetric energy density of hydrogen is relatively low compared to other energy carriers.[2] One approach to address this challenge is the use of liquid organic hydrogen carriers (LOHCs) for chemical hydrogen storage. LOHCs are organic liquids that can chemically bind hydrogen in a reversible manner, which allows for long-term storage and safe transportation of hydrogen under ambient conditions.[3] Benzyltoluene/perhydro benzyltoluene (H0-BT/H12-BT) is a technical LOHC system that is thermally stable, has low toxicity, and has a wide liquid range. It has a hydrogen storage capacity of 6.2 wt%, which is equivalent to 2.1 kWh kg^{-1} or 1.9 kWh L^{-1}.[4] However, to maximize the hydrogen storage capacity and the number of repeated loading and unloading cycles via catalytic hydrogenation and dehydrogenation, respectivly, a superior catalyst selectivity and high conversions are of utmost importance.

Experimental/methodology. In this study, the influence of the support material on the dehydrogenation activity of platinum-based catalyst systems is investigated. Therefore, platinum was supported on a range of materials and the resulting catalysts as well as the support materials were thoroughly characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM) and N_2 physisorption. The dehydrogenation activity was evaluated in semi-batch laboratory-scale dehydrogenation experiments using stirred round-bottom flasks to compare key performance indicators, such as the degree of dehydrogenation (DoDH) of perhydro benzyltoluene and the platinum-based productivity of the catalysts.

Results and discussion. The dehydrogenation performance and catalyst productivity of the prepared catalysts strongly depends on the utilized supports (Fig. 1). These results indicate that the composition, morphology and surface chemistry of the support significantly influence the catalyst activity. Limited pore diffusion and/or insufficient distribution of the active metal over the support surface as well as strong interaction with material additives might hamper the catalysts activity. Overall, this research highlights the importance of understanding how the support material can potentially affect catalyst activity in order to develop more efficient systems in the future.

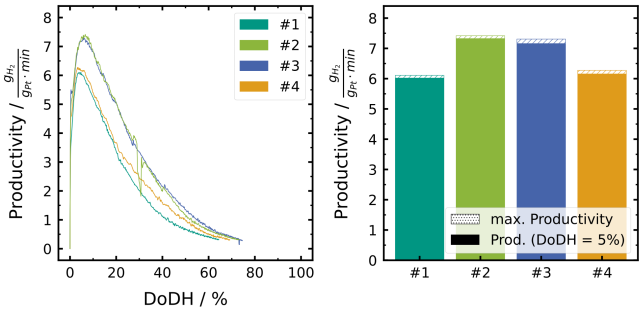

Fig. 1: Productivity (left) and maximum productivity as well as productivity at a DoDH of 5% (right) during semi-batch dehydrogenation of perhydro benzyltoluol with Pt/Al_2O_3 catalysts at 250 °C

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Are zeolites promising supports for diesel oxidation catalysts?

Phuoc Hoang Ho, Derek Creaser, and Louise Olsson*

Chemical Engineering, Competence Centre for Catalysis, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

* *louise.olsson@chalmers.se (Louise Olsson)*

Keywords: Diesel Oxidation Catalysts, Zeolites, High SAR zeolite, Pt-based catalysts

Introduction. Diesel oxidation catalysts (DOC) primarily oxidize CO, unburnt hydrocarbons (HCs), and NO and thereby play a crucial role in meeting emission regulations [1]. Investigating the impact of sulfur poisoning is essential to extend the lifetime of the DOC. Most studies have focused on alumina supports but not zeolites, although zeolites are widely used for other applications in exhaust gas after-treatment systems and are claimed to be promising materials for DOCs in some patents. This work investigates two main aspects on the use of zeolites as supports for DOCs i) different types of zeolites with high siliceous contents in comparisons with alumina support and ii) the effect of Pt/Pd ratio. The activity tests focused on i) the catalytic oxidation of CO, NO, and hydrocarbons (C_3H_8 and C_3H_6) and ii) the deactivation of the oxidation activity of the catalyst during poisoning with SO_2.

Experimental/methodology. High siliceous zeolites (ZSM-5, BEA, and Y zeolites) were used as supports. Monometallic catalysts containing Pt were prepared with a wet impregnation method. A series of Pt-Pd bimetallic catalysts with different Pt/Pd ratios (same amount of total moles of noble metals) was also prepared. Each powder material was subsequently coated on a honeycomb monolith with a dip-coating method. The catalysts were characterized by many techniques including ICP-SFMS, XRD, HRTEM, N_2 physisorption, CO chemisorption, and DRIFTS.

Results and discussion. Pt dispersion was ranked in the order of Pt/Y (4.6%) < Pt/Al_2O_3 (6.5%) < Pt/BEA (7.3%) ~ Pt/ZSM-5 (7.4%), resulting in an average particle size range of 15 – 24 nm. The Pt/BEA catalyst not only decreased the T_{50} for CO and C_3H_8 oxidation compared to the benchmark Pt/Al_2O_3 catalyst (Fig. 1a) but also showed a more stable conversion. All zeolite-based catalysts had significantly lower T_{50} values for C_3H_8 oxidation, perhaps due to better confinement of C_3H_8 in the zeolite pores than in alumina. During the SO_2 poisoning, the Pt/BEA showed more stable conversions than Pt/Al_2O_3 for CO and C_3H_6 but faster deactivation partially for NO oxidation, due to the low sulfur adsorption capacity of the support. The addition of 20 ppm SO_2 promoted C_3H_8 oxidation for both Pt/Al_2O_3 and Pt/BEA, but the SO_2 promotion for C_3H_8 oxidation occurred faster on the latter than the former (data not shown here). The addition of a small fraction of Pd improved the oxidation resistance of Pt and this enhanced the oxidation of CO and C_3H_6 as well as the reduction of NO with hydrocarbon. The Pt3Pd1/BEA showed also better sulfur resistance for CO oxidation than the monometallic Pt catalyst (Fig. 1b).

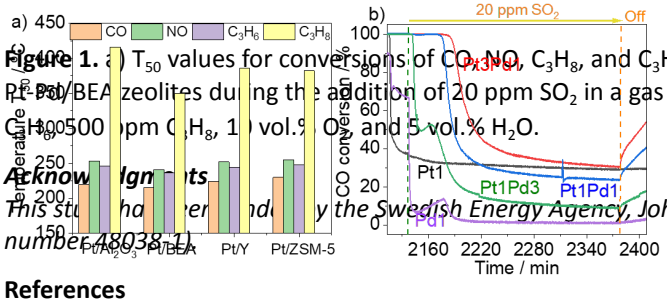

Figure 1. a) T_{50} values for conversions of CO, NO, C_3H_8, and C_3H_6 with different catalysts and b) effect of Pt/Pd ratios on Pt-Pd/BEA zeolites during the addition of 20 ppm SO_2 in a gas mixture containing 1000 ppm CO, 500 ppm NO, 500 ppm C_3H_6, 500 ppm C_3H_8, 10 vol.% O_2 and 5 vol.% H_2O.

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Pd-Catalyzed direct C-H Carboxylation of Arenes with Carbon Dioxide

G. Kemper[1,2], M. Hölscher[1*], W. Leitner[1,2*]

[1]*Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Aachen, Germany*
[2] *Max-Planck-Institut für chemische Energiekonversion, Mülheim (Ruhr), Germany*
[*]*walter.leitner@cec.mpg.de,* [*]*hoelscher@itmc.rwth-aachen.de*

Keywords: Catalysis, Palladium, Carboxylation, CO_2

Introduction

Targeting a circular and sustainable production of chemical goods, the utilization of the nonfossil and nontoxic low value "waste" material carbon dioxide (CO_2) has the potential to play a key role in designing future processes and chemicals. Among the many interesting and challenging reactions with CO_2 the direct C-H carboxylation of arenes, enabled by only catalytic amounts of organometallic compounds, remained unsolved so far. This reaction, which is therefore often referred as *dream reaction*, represents a highly atom efficient procedure for the generation of aromatic carboxylic acids - the latter being a frequent motive in high value chemicals. Accordingly, this catalytic reaction provides the potential to satisfy most of the principles of green chemistry; especially when achieving high turnover numbers, chemo- as well as regioselectivity and the avoidance of additional solvents and additives.

Experimental/methodology

In recent years we have conducted various computational and experimental studies[1] to develop active molecular catalysts for the carboxylation of arenes with CO_2 and have recently reported on a stochiometric reaction.[2] In this work, we present a thorough experimental study on the direct carboxylation of a variety of arenes together with detailed DFT studies for one exemplified substrate.[3]

Results and discussion

We show that with sulfonamidophosphane ligands surprisingly active Pd-catalysts can be synthesized and applied in direct carboxylations of CO_2. The results of catalytic carboxylations for various arenes are reported. Both experiments and DFT studies show that electron rich arenes are carboxylated easily, while electron poor substrates undergo the reaction with low conversion.

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Synthesis of graphene supported efficient nano-catalysts for biomass applications

Will Chartier

Loughborough University, Loughborough, United Kingdom
w.chartier@lboro.ac.uk

Keywords: Net zero carbon, graphene oxide

Introduction. Biotechnology needs to play a major role in the transition from our current fossil-fuel reliant society towards a lower-carbon and sustainable economy. The grand challenge centres around the fundamental science differences between dilute aqueous biorefinery streams containing organic/biological molecules and concentrated long chain species in crude oil. For materials at nanoscale, novel electronic structures are strongly impacted by the dimension and morphology of the materials generated. Metallic nanoparticles contained in a 2D membrane allows the study of catalysis under nanoconfinement and realization of the dual system for both precise molecular separation and nano scale catalysis.

Experimental/methodology. Synthesise graphene oxide supported catalysts including Ni, Pt, Ni-Pt alloys with controlled particle size and morphology for biomass applications via microwave and hydrothermal approaches. Understand the mechanisms of the synthesis and catalysis of these developed graphene supported catalysts. Investigate the effects of reaction conditions of both microwave and hydrothermal synthesis with a combination of both methods on the particle size and morphology of Ni, Pt and alloy particles with the reduction of graphene oxide. Investigate the effects of reaction conditions on the formation of graphene oxide supported Ni, Pt and alloy catalysts, to characterise particle size, morphology, crystal structures distribution of particles on graphene oxide, catalytic activity of the catalysts, reduced graphene oxide (rGO) and rGO supported catalysts synthesised.

Results and discussion. Graphene oxide supported metal catalysts investigated under SEM and EDX microscopy where nickel nanoparticle aggregations were found. The crystallite size varies depending on the reducing agent used and their sizes vary between 15 and 21nm. Further characterisation by XRD and UV-Vis show the sucessful synthesis of nickel from precursors. 4- Nitrophenol to 4- Aminophenol catalytic conversion experiments characterised by UV-Vis show good catalytic reduciton of graphene oxide suppported platinum and nickel catalysts.

Acknowledgments
SlowCat, Dr Xujin Bao, Dr Kenny Jolley, Dr Simon Kondrat

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The name of presenting author should be underlined.

Mesoporous Silica Monoliths as Porous Scaffold for Heterogeneous Organocatalysis in Continuous-flow

U. Ali[1], Peter R. Schreiner[2], Bernd M. Smarsly*[1]

[1]*Institute of Physical Chemistry, Justus Liebig University, Giessen, Germany*
[2]*Institute of Organic Chemistry, Justus Liebig University, Giessen, Germany*
[*]*Bernd.Smarsly@phys.chemie.uni-giessen.de*

In organic chemistry for synthesis of organic compounds, we need a lot of apparatus, reagents, catalysts and specific conditions so that at the end we get mixture of products, side products, mixed catalysts and then we need to separate this mixture from each other. This complicated and time-consuming process is known as batch synthesis. To minimize all these flaws and synthesizing product through simple and straight forward way to get maximum yield that can be collected easily without further purification, the concept of "Synthesis in Continuous-Flow" is established and attracted great attention in chemical societies. In this project we worked on tuning of mesoporous space in silica monoliths that are being used as porous scaffold for heterogeneous catalysis in continuous-flow. We carefully tuned the hydrothermal temperature during synthesis of silica monoliths and exclusive but detailed physisorption studies confirmed the orderly tuning of mesopore space from restricted mesopores to well-connected open mesoporous system. The mesopore size is controlled form 11nm to 15nm with difference of 1 nm by changing hydrothermal temperature 80°C to 95°C by gape of 3°C. The further change of mesopore size from 15nm to 27nm is controlled by using hydrothermal temperature range of 95°C to 110°C with change of 5°C. The resulting monoliths with known mesopore space were functionalized with thiourea catalyst and heterogeneous flow catalysis performed on a very classic reaction used for protection of alcohols and phenols with 3,4-dihydro-2*H*-pyran. By using immobilized thiourea catalyst on silica monoliths, very fine yields were achieved in number of reactions by varying different alcohols protection by 3,4-dihydro-2*H*-pyran.

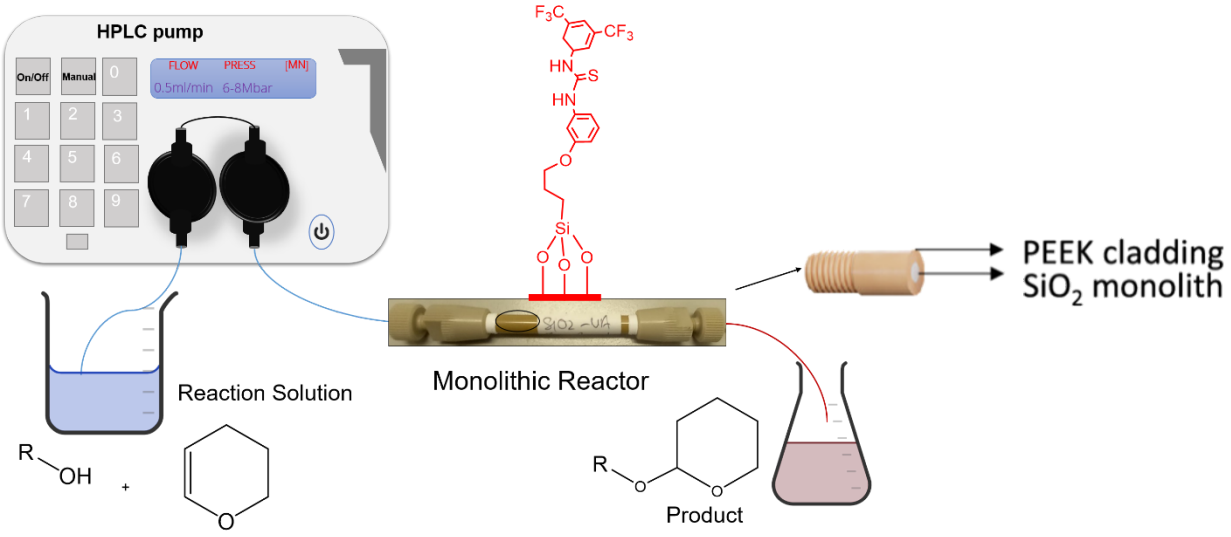

Figure 1: Flow catalysis setup for protection of alcohol with 3,4-dihydro-2H-pyran by using thiourea catalyst immobilized on silica monolith.

Ammonia decomposition over transition-metal/carbon catalyst for on-site generation of hydrogen

Zongkun Chen*, Michael Poschmann, Natalia Kowalew, Marius Heise-Podleska, Tobias Stamm, Robert Schlögl, Saskia Heumann*

Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr/Germany
**saskia.heumann@cec.mpg.de*

Keywords: ammonia decomposition, carbon, hydrogen

Introduction. The Catalytic decomposition of ammonia with complete conversion to hydrogen production at low temperature has received extensive attention because on-site hydrogen production from ammonia bypasses the challenges of hydrogen storage and transportation. Among various technologies for the production of hydrogen via ammonia decomposition, thermal decomposition is the most common technique [1], which is usually carried out at higher temperatures. Considering that decreasing the conversion temperature to increase the conversion efficiency is beneficial for facilitating the further development of this field, numerous efforts have been devoted to the development of highly active and robust catalysts [1, 2]. State-of-the-art ammonia decomposition catalysts are ruthenium doped with potassium, barium, and cesium and supported on various oxides and carbon supports [3]. However, these catalysts are still insufficiently active for low-temperature NH_3 decomposition and, more importantly, for large-scale applications it is not economically feasible. Considering that a satisfactory performance-to-cost ratio could make the catalysts stand out from the competition with their counterparts, it is urgent to incorporate both performance and cost into their design and fabrication. In our study, transition-metal oxides or transition-metal have been supported onto carbon materials as the potential catalysts for the decomposition of ammonia by a facile freeze-drying and calcination method.

Experimental/methodology. Figure 1A schematically illustrates the facile freeze-drying and calcination method that could effectively fabricate transition-metal/carbon catalyst with a hierarchical structure, which mainly involves freezing a mixture of glucose and Na_2CO_3 in aqueous solution, followed by the freeze-drying of the mixture and subsequent pyrolysis at certain temperatures to obtain the desired carbon materials with hierarchical structure.

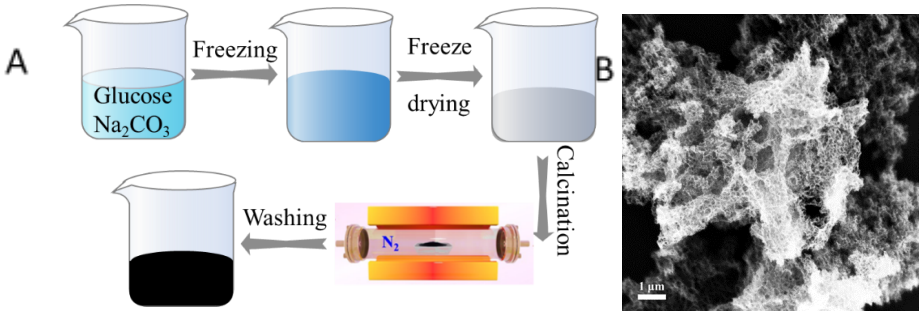

Figure 1. (A) A schematic illustration of the synthetic strategy for carbon materials with a hierarchical structure. (B) SEM image of the obtained carbon materials.

Results and discussion. As shown in Figure 1B, the structure of the obtained carbon materials can be considered as the aggregation of numerous interconnected hollow carbon bubbles with a size of 100-200 nm, leading to a 3D porous carbon with very open access. The material properties of the hierarchical carbon materials are modified by systematically varying the synthesis parameter, such as temperature or reactant ratios. The structure-property correlations are investigated in dependence of ammonia decomposition with the focus on activity, selectivity and stability.

Acknowledgments
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Activity and stability of the catalytic oxidation of methane with Pd/CeO_2 nanorods, nanocubes, and octahedra

M. C. Policano*, L. Lefferts, J. A. F. Albanese

Catalytic Processes and Materials Group, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

**Corresponding Author's E-mail address: m.chiquettopolicano@utwente.nl*

Keywords: Methane oxidation, CeO_2, structure, activity, poison resistance

Introduction. More restrictive regulations aimed at drastically reducing the emissions of harmful and greenhouse gases (GHG), triggering a shift in the maritime industry. Given this, the use of liquified natural gas (LNG) powered vessels instead of e standard heavy fuel oil (HFO) can contribute to reductions in SO_2, NO_X, CO_2, CO, and toxic particles[1]. However, this reduction comes with an increase of around 5 times in methane emissions[1], which is highly undesirable as the methane global warming potential (GWP) is 37±10 in a 100-year horizon[2]. Oxidation of unburnt methane on palladium-based catalysts is an attractive proposition for the reduction of GHG emissions in LNG engines as it can achieve high conversion levels at low temperatures and short contact times[3]. Despite the high activity of palladium-based catalysts in dry conditions, the addition of water can deactivate the catalyst due to the formation of $Pd(OH)_2$ and hydroxyl accumulation on the support, which consequently hinders oxygen mobility[4]–[6]. Considering that water is generated during methane combustion, the development of water-resistance catalysts is key for large-scale deployment. To overcome this challenge one can leverage the high oxygen mobility of supports such as CeO_2 that can increase the activity of oxidation catalysts, reducing the impact of water on oxygen availability[6]. Different morphologies of CeO_2 create different facet terminations affecting the Pd oxidation state and CeO_2 reducibility[7]. This work aims at studying the methane oxidation activity and water resistance of different CeO_2 facet terminations: nanorods {111}, nanocubes {100}, and octahedrons {110} and {111}.

Experimental/methodology. The CeO_2 supports with different morphologies were synthesized using a hydrothermal method[8] followed by wet impregnation of Pd to achieve a 5 wt. % loading. Methane (400-4000 ppm) and water (0-10 %) concentrations were varied at 10 vol. % oxygen. Product distributions were measured using on-line gas chromatography (Varian CP-3800). Detailed catalyst characterization vias: TEM, SEM, XRD, and Raman were conducted to build property-structure-activity-stability relationships.

Results and discussion. Reactions with different methane and water concentrations at different temperatures allow the unveiling of reaction orders of methane and water with each CeO_2 support. Moreover, time-on-stream experiments provided information about the stability of the catalysts in dry or wet conditions. By combining the reaction kinetics data with the catalyst characterization it will be possible to elucidate the factors that control the activity and stability of facetted Pd-CeO_2 catalysts.

Acknowledgments. This work was supported by the LNG-Zero project; grant number 20002675-10.

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Selective oxidation reaction using MAX phases as heterogeneous catalysts

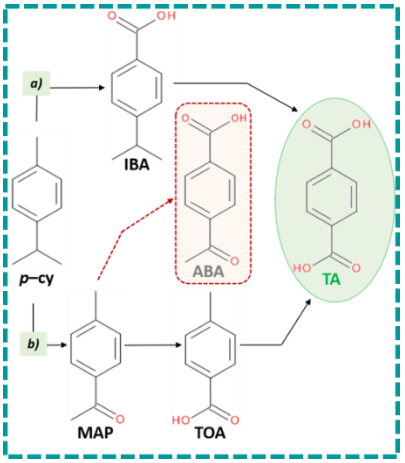
Iuliana M. Chirica[1,2*], Mihaela M. Trandafir[1], Anca G. Mirea[1], Florentina Neațu[1], Ștefan Neațu[1], Michel W. Barsoum[3], Mihaela Florea[1]

[1] *National Institute of Materials Physics, 405A Atomistilor Street, 077125 Magurele, Romania*
[2] *University of Bucharest, Faculty of Physics, 405 Atomistilor Street, 077125 Magurele, Romania*
[3] *Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania 19104, USA*
[*] *iuliana.bogdan@infim.ro*

Introduction. A focused research in the last decades showed that the scientific community handled an important challenge to identify the next generation of sustainable, cost-effective and energy efficient catalytic materials [1]. Selective oxidation reactions of hydrocarbons continue to be in the spotlight of both academia and industry [2] and play a key role for the production of valuable compounds [3] used in important fields, ranging from polymer synthesis to medicinal chemistry. [4]

Experimental/methodology. In this line, selective oxidation of *p*-cymene is an important green industrial chemical process due to the fact that represent a viable alternative to the oxidation of *p*-xylene to terephthalic acid (TA), one of the monomers used for the production of polyethylene terephthalate (PET) [5]. Moreover, other reaction oxidation products, such as *p*-methylacetophenone (MAP), *p*-toluic acid (TOA) and *p*-isopropylbenzoic acid (IBA) have applications in various fields [6].

Results and discussion. In this study, the catalytic properties of different MAX phases (Ti_3AlC_2, Ti_2AlC, V_2AlC, Ti_3SiC_2, Mo_2Ga_2C and $Mo_2Ti_2AlC_3$) were investigated in catalytic oxidation reaction of *p*-cymene (see Scheme 1), with remarkable results obtained only in the case of Ti_3AlC_2, Ti_2AlC and Ti_3SiC_2, respectively. The highest obtained yield of ~41% in terephtalic acid was achieved at 140 °C and 2.3 MPa O_2 pressure on Ti_3AlC_2. With the MAX phase acting as catalyst, the selective oxidation occurred at the methyl substituent as well as at the isopropyl substituent through two different reaction pathways (***Scheme 1***, ***a)*** and ***b)***), generating several reaction products, identified by ^{1}H–RMN. Therefore, MAX phases present good activity in p-cymene oxidation reaction, and moreover MAX phase compositions are stable in the reaction conditions used, as evidenced by the Raman and X-ray diffraction data recorded before and upon testing.



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Different reaction pathways for the oxidation of p-cymene

Acknowledgments

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Formation of oxygen vacancies and their role in $LaCoO_3$ perovskite catalysts for CO oxidation

J. Cho[1], S. Kim[1], M. Kim[1], K.T. Park[2], H.W. Park[3], J.C. Jung[1*]

[1]*Department of Chemical Engineering, Myongji University, Yongin, 17058, Republic of Korea*
[2]*Iron & Steel Process Engineering Research Group, POSCO, Pohang, 37859, Republic of Korea*
[3]*Hydrogen Research Center, Research Institute of Industrial Science & Technology (RIST), Pohang, 37673, Republic of Korea*
[*]*jcjung@mju.ac.kr*

Introduction.

Surface defects, such as oxygen vacancies, of perovskite oxides can be easily controlled through various methods due to their high design flexibility [1]. Particularly, when using perovskites as heterogeneous catalysts for various oxidation reactions, formation of the surface oxygen vacancies strongly affect their catalytic activity. In this study, we synthesized $LaCoO_3$ catalysts and induced oxygen vacancies through post-treatments (acid or reductive thermal treatments). Additionally, non-stoichiometric $LaCoO_3$ perovskites were also prepared to control their oxygen vacancies. Through this work, the effect of the post-treatments and non-stochiometry on the surface properties and the catalytic activities of $LaCoO_3$ perovskites in CO oxidation was systematically investigated using various characterizations.

Experimental/methodology.

$LaCoO_3$ perovskite was synthesized through a citrate sol-gel method. Then, as-prepared $LaCoO_3$ was soaked in diluted HNO_3 solution for 1, 5, and 12 h, respectively, for the acid treatments. In the reductive thermal treatment procedure, $LaCoO_3$ was loaded in a continuous-flow fixed-bed reactor and heated under 4% H_2/N_2 flow at 200 and 400 °C, respectively. Non-stoichiometric $LaCoO_3$ perovskites with Co/La ratios of 0.9 and 0.95 were also prepared through the citrate sol-gel method.

Results and discussion.

According to previous studies, the properties of surface oxygen species (surface lattice oxygen (O_{lat}) and adsorbed oxygen species (O_{ads}) on oxygen vacancies) significantly influence the catalytic behavior in CO oxidation [2]. Therefore, the effect of post-treatments and non-stoichiometry on the chemical species of $LaCoO_3$ was examined through X-ray photoelectron spectroscopy. Based on the experimental results, we investigated the correlation between the surface chemical state (O_{ads}/O_{lat} and Co^{2+}/Co^{3+}) and the reaction temperature at which the CO conversion reaches 50% (T_{50}) to elucidate their relationship. As shown in Fig. 1, the catalytic activity of the prepared catalysts in CO oxidation enhanced as the O_{ads}/O_{lat} and Co^{2+}/Co^{3+} increased. Consequently, we confirmed that surface oxygen vacancies formed in post-treated and non-stoichiometric $LaCoO_3$ catalysts facilitate the conversion of CO to CO_2.

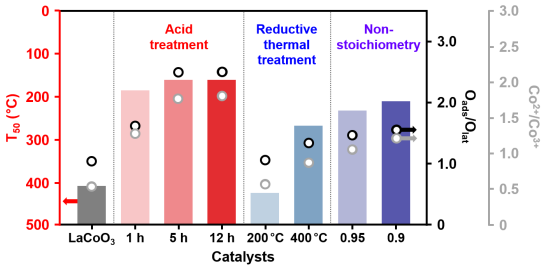

Fig. 1. Correlation between the surface chemical state (O_{ads}/O_{lat} and Co^{2+}/Co^{3+} ratio) and the catalytic activity (T_{50}).

Acknowledgments

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Highly selective CO_2 fixation reaction over single-Ta-substituted Lindqvist-type hexaniobate cluster as base catalyst

V. Chudatemiya[1], M. Tsukada[1], H. Nagakari[1], S. Kikkawa[1], N. Nakatani[1], S. Yamazoe[1,2*]

[1]*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Tokyo, Japan*
[2]*Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, Tokyo, Japan*
[*]*yamazoe@tmu.ac.jp*

Keywords: metal oxide cluster, base catalysis, CO_2 fixation

Introduction. Recently, the application of metal oxide clusters as base catalysts has been reported, while those materials have been known for acid catalysts, photocatalysts, and redox catalysts[1],[2]. We have reported the base catalysis of Lindqvist-type V-group metal oxide clusters $[M_6O_{19}]^{8-}$ (M = Nb, Ta) for Knoevenagel condensation reaction and CO_2 fixation reaction due to the highly negative natural bonding charge of the surface O atoms[3]. In this study, tetrabutylammonium (TBA) salts of $[Ta_xNb_{6-x}O_{19}]^{8-}$ (TBA-Ta_xNb_{6-x}, x = 0−6), were prepared and applied as the catalysts for CO_2 fixation to styrene oxide (**SO**) for tuning the selectively toward styrene carbonate (**SC**).

Experimental/methodology. TBA-Ta_xNb_{6-x} were synthesized by a microwave-assisted hydrothermal method in tetrabutylammonium hydroxide aqueous solution according to the literature[4],[5]. The fabricated clusters were characterized by ESI-MS, FT-IR, elemental analysis, and XAFS analysis, and the adsorption energy was calculated by DFT calculation. CO_2 fixation to **SO** were carried out in a batch-type reactors under atmospheric gas pressure. The reaction solutions were analyzed by GC-FID and GC-MS using an internal standard.

Results and discussion. The clusters were employed as the catalysts in CO_2 fixation to **SO** (Figure 1). **SO** conversion increased with higher Ta content, however, the selectivity toward **SC** depended on the composition of the clusters. The viscosity of the product solution gradually increased with higher Ta content, indicating the polymerization of **SO** as a side reaction. Interestingly, single-Ta-substituted TBA-Ta_1Nb_5 maintained the high **SC** selectivity even at a high **SO** conversion. XAFS and DFT studies revealed that the adsorption of **SO** and CO_2 preferentially occurred on the terminal O coordinated to Ta over that of Nb and the adsorption energy of CO_2 was lower than that of **SO**. Thus, the undesiable polymerization occurred over Ta-rich TBA-Ta_xNb_{6-x}, while the single Ta site promoted CO_2 activation and the following nucleophilic attack to **SO** to form **SC.** In this work, the highest selectivity of **SC** could be achieved using single-Ta-substituted TBA-Ta_1Nb_5 as the catalyst.

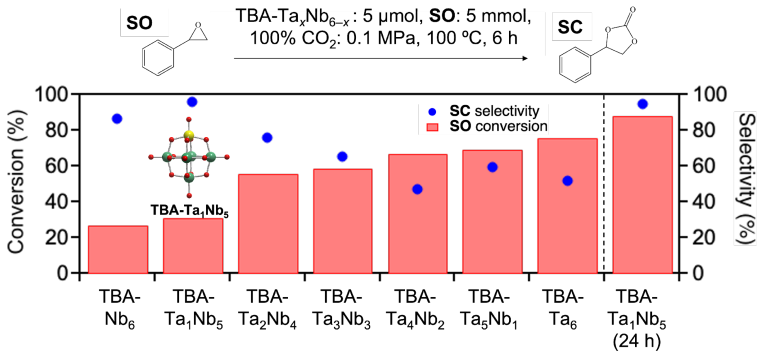

Figure 1. CO_2 fixation to SO over TBA-Ta_xNb_{6-x}. Bars and dots represent SO conversion and SC selectivity, respectively.

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An Adaptive Rhodium Catalyst to Control the Hydrogenation Network of Nitroarenes

V. Chugh,[1,2] B. Chatterjee,[1,2] W.C. Chang,[1,2] H. H. Cramer,[1] H. Randel,[1,2] C. Hindemith,[1,2] T. Weyhermüller,[1] C. Farès,[3] and C. Werlé[1,2*]

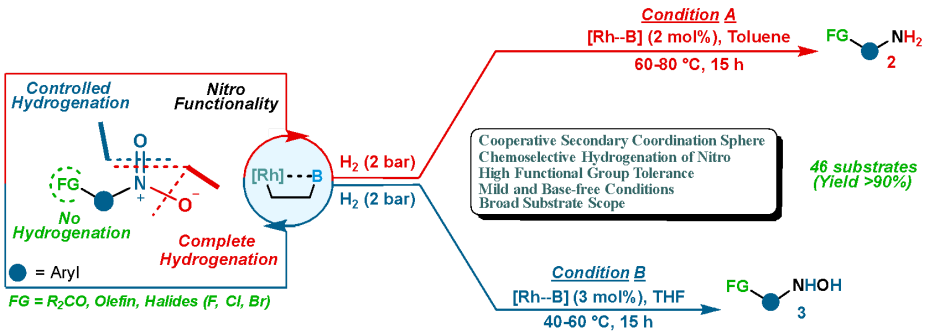
1. Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany.
2. Ruhr University Bochum, Universitätsstr. 150, 44801 Bochum, Germany.
3. Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany.

Keywords: Hydrogenation, Adaptive Catalysis, Hydroxylamines, Anilines, Nitroarenes

Introduction. Catalysts and catalytic systems are typically used to transform substrates selectively into a single product.[1] Alternatively, one could imagine dynamic catalytic systems that adapt to the reaction conditions—allowing precise control over bond activation processes and catalytic sequences—to yield distinct products.[2] In this context, reducing nitro compounds on the way to fully reduced aniline might lead to several potentially useful platforms, provided selectivity can be controlled.[3,4]

Experimental/methodology. Experimental mechanistic studies and DFT calculations revealed: 1) the importance of the designed ligand environment for providing the catalyst with adaptive properties; 2) the role of the solvent medium in controlling the selectivity of the catalyst; 3) the formation of a rhodium-hydride intermediate capable of 4) transferring the hydride to the boron-activated substrate site.

Results and discussion. An adaptive rhodium-based catalytic system for the controlled hydrogenation of nitro-containing substrates to anilines and hydroxylamines will be presented. The system employs a rhodium(III) center with a Lewis acidic boron arm in the secondary coordination sphere to control the catalytic network.[5]



Acknowledgments

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Photocatalytic oxidation of aromatic alcohols to aromatic ketones over non-toxic dye-sensitized photocatalysts

S. Imai[1], S. Yuka[2], A. Onda[2,3], K. Imamura[2,3*]

[1]*Graduate School of Integrated Arts and Sciences, Kochi University, Kochi, 780-8520, Japan*
[2]*Faculty of Science and Technology, Kochi University, Kochi, 780-8520, Japan*
[3]*Research Laboratory of Hydrothermal Chemistry, Kochi University, Kochi, 780-8520, Japan*
[*]*imamura-kazuya@kochi-u.ac.jp*

Keywords: dye-sensitized, photocatalyst, visible light, photocatalytic oxidation

Introduction. Photocatalytic reaction is redox reaction caused by only photoirradiation, i. e., photocatalytic reaction proceeds at room temperature and under atmospheric pressure. Therefore, many researcher have been studied have been studied application of photocatalytic reaction to organic synthesis. Most of them, titanium(IV) oxide (TiO_2), which have high photocatalytic activity and chemical stability, was used as photocatalyst. However, TiO_2 is driven only by ultraviolet light, which is rarely contained in sunlight. For using sunlight effectively, visible-light driven photocatalyst is favorable. Dye-sensitized TiO2, in which a dye is adsorbed on the surface of TiO_2, is a visible light responsive photocatalyst [1]. Generally, expensive noble metals such as ruthenium (Ru) and iridium (Ir) are used as dyes for sensitizer. In addition, leaching of them causes a environmentally problem. In this study, dye-sensitized photocatalysts using fluorescein, non-toxic dye to the environment and human, have been prepared and successfully applied to the photocatalytic oxidation of 1-phenylethanol to acetophenone.

Experimental/methodology. Bare TiO_2 was suspended in ethanol solution containing fluorescein and stirred at room temperature for overnight. Fluorescein adsorbed TiO_2 (Fl-TiO_2, 50 mg) was suspended in acetonitrile solution (5 cm^3) containing 1-phenylethanol (ca. 50 μmol) in a test tube. After gas phase was replaced by dioxygen (O_2) and sealed with a rubber septum, the test tube was photoirradiated by Green LED (λ_{max} = 550 nm). After photoirradiation, the catalyst was removed by filtration, liquid phase was analyzed by liquid chromatography.

Results and discussion. Fig. 1 shows time courses of the amount of 1-phenylethanol remained and acetophenone formed. The amount of 1-phenylethanol decreased with photoirradiation, while the amount of acetophenone increased. After 1.5-h photoirradiation, acetophenone was obtained in a high yield 94 %. After the reaction, photocatalyst was eliminated by centrifugation from reaction mixture. Recovered photocatalyst was reused at least three times without loss of activity.

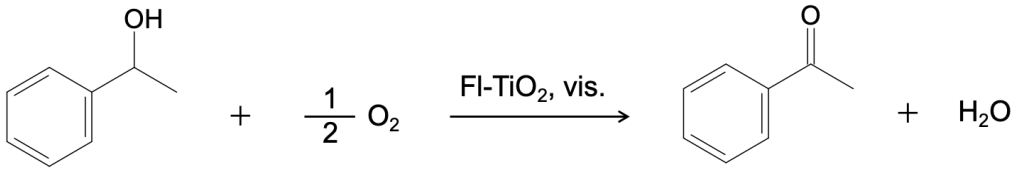

Figure 1. Photocatalytic oxidation of 1-phenylethanol to acetophenone over fluoresceine-modified TiO_2 (Fl-TiO_2) under visible light.

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Cooperative Catalysis between Au Nanoparticles and Metal Oxides for Rapid C–B Bond Formation

K. Imoto[1], H. Miura[1,2,3*], A. Junkaew[4], M. Ehara[3,5], T. Shihido[1,2,3]

[1]*Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan*

[2] *Research Center for Hydrogen Energy-Based Society, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan*

[3] *Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8520, Japan*

[4] *National Nanotechnology Center, 111 Innovation Cluster 2 Thailand Science Park, Phahonyothin Rd., Khlong Nueng, Khlong Luang, Pathum Thani, Thailand*

[5] *Institute for Molecular Science, 38 Myodaizicho Nishigonaka, Okazaki, Aichi 444-0867, Japan*

[*]*miura-hiroki@tmu.ac.jp*

Keywords: Au Nanopariticle, Cooperative Catalysis, Borylation

Introduction.

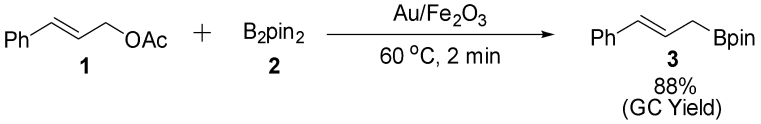
Cooperative catalysis between metal nanoparticles and the support enables the efficient transformation of organic molecules. Therefore, elucidation of the relationship between catalytic activity and the cooperation of metal nanoparticles and supports is important for catalyst design. We reported that supported Au nanoparticle catalysts showed high activity for borylation of allylic C(sp^3)–O bond to give allyl boronates.[1] In this study, we investigated the relationship between catalytic activity for borylation of C(sp^3)–O bond over supported Au catalysts and their physical properties.

Experimental/methodology.

Supported Au catalysts were prepared through deposition-precipitation method by using tetrachloroauric acid as an Au precursor and urea as a pH adjust reagent. The specific surface area and acidity of the catalysts were determined from nitrogen adsorption/desorption isotherms and pyridine adsorption FT-IR spectra, respectively.

Results and discussion.

The allylic borylation of cinnamyl acetate (**1**) with B_2pin_2 (**2**) at 60 °C in the presence of Au/Fe_2O_3 catalyst completed within only 2 min to give the desired cinnamyl boronate (**3**) in high yield (Scheme 1). Kinetic study revealed that carbocations formed as intermediates, and that the activation of B_2pin_2 by Lewis acid on support was the rate-determining step. Moreover, a positive correlation was observed between the amount of Lewis acid per unit surface area (acid density) and TOF (Fig. 1). These results suggest that both Au nanoparticles and Lewis acid at the surroungings of Au nanoparticles cooperatively activated the substrates. Therefore, the use of catalysts with high Lewis acid density is essential for efficient cooperative activation of organic molecules.



Scheme 1. Borylation of cinnamyl acetate by Au/Fe_2O_3

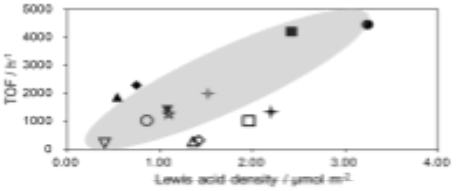


Fig. 1.Relationship between activity and Lewis acid density of various metal oxides.

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Decoration of Au/SiO_2 by Thin Metal Oxide Layer Derived from Layered Double Hydroxides

K. Okayama[1], A. Nakayama[1], T. Murayama[1], N. Sakaguchi[2], T. Shimada[1], S. Takagi[1], T. Ishida[1,*]

[1]*Department of Applied Chemistry for Environment, Tokyo Metropolitan University, Tokyo, Japan*
[2]*Center for Advanced Research of Energy and Materials, Hokkaido University, Hokkaido, Japan*
[*]*Corresponding Author: tamao@tmu.ac.jp (T. Ishida)*

Keywords: Gold nanoparticles, Layered Double Hydroxide, CO oxidation, PROX

Introduction. Recently, decoration of metal nanoparticle (NP) surface by thin metal oxide (MOx) layers has been intensively studied to create new Au–MOx interface on metal NPs. However, the conventional methods have some problems such as limitation of the types of MOx, difficulty in controlling the thickness of the MOx layer, and the need for expensive apparatus. In this study, we focused on layered double hydroxides (LDHs) as a coating material for supported Au catalysts. LDHs ($[M(II)_{1-x}M(III)_x(OH)_2][(A^{n-})_{x/n}\cdot yH_2O]$) are consisted of a divalent metal hydroxide and M(III) is partly replaced. LDHs can be exfoliated into LDH monolayer nanosheets (NS) and is converted to a mixed metal oxide (MMO) by calcination. In this work, LDH NS is used as a precursor for the decoration of Au surface by thin MMO layer (Fig. 1). We found that the modification of Au NPs by LDH NS can create effective Au–MOx interface on Au NPs, and the catalytic activity of the obtained catalysts for CO oxidation was greatly improved.

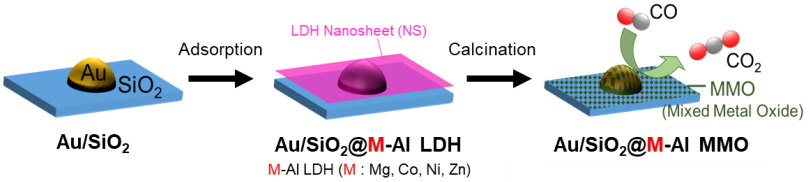

Fig. 1 Schematic image of mixed metal oxide-decorated Au/SiO_2 using LDH nanosheets.

Experimental. Au/SiO_2 (1 wt% of Au loading, 5.8 nm of Au NPs) was purchased from Haruta Gold Inc. Four kinds of LDHs (Mg-Al, Zn-Al, Co-Al, Ni-Al) were prepared by homogeneous precipitation method using urea according to the previously report.[1] The LDHs were exfoliated according to the literature to give LDH NS. The monolayer LDH NS was adsorbed on Au/SiO_2 ($Au@SiO_2@LDH$) followed by calcination in air to give Au/SiO_2@M-Al MMOs. For comparison, Co-Al oxides were deposited on Au/SiO_2 by impregnation to give Co-Al/Au/SiO_2-imp. Catalytic performance of the catalysts was evaluated by CO oxidation in a fixed bed flow reactor (1 vol% CO in air, SV=20,000 mL g_{cat}^{-1} h^{-1}).

Results and discussion. Structures of LDHs and exfoliation of LDHs were confirmed by XRD. TEM-EDX analysis of Au/SiO_2@M-Al LDHs revealed that the metals derived from LDHs were highly dispersed on the entire catalyst surface. TEM images also confirmed the formation of the overlayer with the thickness of ca. 1 nm on Au/SiO_2. The CO oxidation was carried out using Au/SiO_2@Co-Al LDH. The CO conversion increased rapidly at about 250 °C in the first run, which coinsides the conversion of LDH to MMO (Fig. 2). While cooling the catalyst from 330 °C, the full conversion was maintained even at 50 °C. Given that the CO conversion of Au/SiO_2 was only 24 % at 303 °C, the activity was significantly improved by modification of Au/SiO_2 with Co-Al MMO. The catalytic activity order of Au/SiO_2@M-Al MMO was M=Co> Ni>Zn>Mg. Au/SiO_2@Co-Al MMO showed higher activity than Co-Al/Au/SiO_2-Imp. The results suggest that covering Au surface by thin MMO layer was more efficient to create new Au-CoOx interface than the deposition of Co-Al oxides by impregnation.

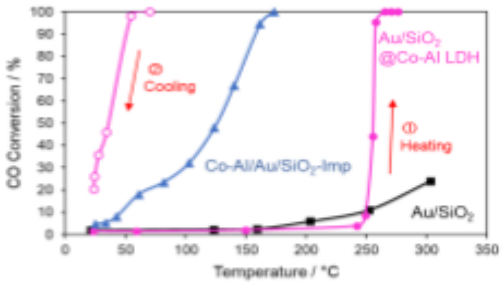

Fig. 2 CO oxidation of Au/SiO_2@Co-Al LDH.

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Acid Catalysis over Crystalline Zr_3SO_9: Role of the Local Structure in Generating Acidity

Satoshi Ishikawa[1]*, Meilin Tao[1], Takuji Ikeda[2], Shunsaku Yasumura[3], Kosuke Shimoda[3], Ryota Osuga[4], Yuan Jing[3], Takashi Toyao[3], Ken-ichi Shimizu[3], Hiromi Matsuhashi[5], Wataru Ueda[1]

[1]*Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan*
[2] *Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Sendai 983-8551, Japan*
[3] *Institute for Catalysis, Hokkaido University, N-21, W-10 Kita-ku, Sapporo 001-0021, Japan*
[4] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-2-1 Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan*
[5] *Department of Science, Hokkaido University of Education, 1-2 Hachiman-cho, Hakodate, Hokkaido 040-8567, Japan*
sishikawa@kanagawa-u.ac.jp

Keywords: sulfated zirconia catalyst, local structure, acid catalysis

Introduction. Sulfated zirconia (ZrS) is widely known to exhibit an excellent catalytic activity for various acid reactions. Fundamental understanding of its outstanding acidity can offer a way for rational catalyst design. However, its catalytically active structure has yet to be identified to date, due to the inhomogeneity of the catalyst state. In this study, we focused on the crystalline Zr_3SO_9 catalyst reported 30 years ago by Kato *et al.*[1]

Experimental/methodology. Crystalline Zr_3SO_9 was synthesized by hydrothermal method according to the procedure reported by Kato *et al*.[1] Briefly, the precursor solution prepared by dissolving $ZrOCl_2 \cdot 8H_2O$ (Zr: 7.5 mmol) in H_2SO_4 (15 mmol) containing 14 mL distilled water was hydrothermally treated at 240 °C for 72 h to obtain Zr_3SO_9.

Results and discussion. The Crystal structure of Zr_3SO_9 was solved by combining the results of elemental analyses, microscopic analyses, and *ab-initio* structural analysis using the powder XRD pattern. Zr_3SO_9 consisted of the sheet having the same structural arrangement of (101) plane of the tetragonal ZrO_2, and SO_4^{2-} was uniformly isolated on the Zr trimer (Fig. 1). This material exhibited outstanding catalytic activity for various acid reactions, and the activity was far better than those of typical acid catalysts including ZrS. In the isomerization of *n*-butane in which super acidity is needed for catalysis, the catalytic activity of Zr_3SO_9 was 2.5/7.5 times higher than those of ZrS in the catalyst amount/S amount basis.

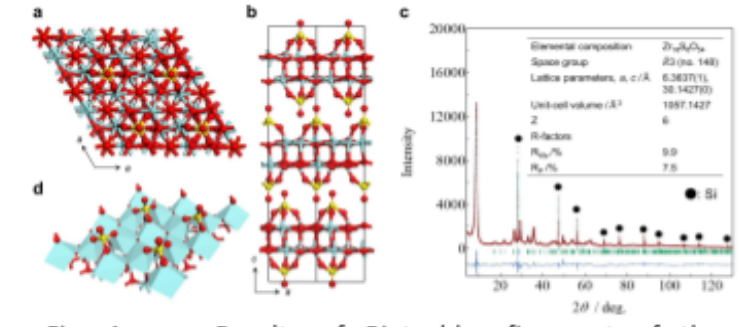

Fig. 2. Local structure of the crystalline Zr_3SO_9 in generating acidity.

Spectroscopic analyses and DFT calculations revealed that the Zr site adjacent to SO_4^{2-} acts as the Lewis acid site, and H_2O coordinated on this Zr site acts as the Brønsted acid site (Fig. 2).

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A Innovative 3D Printed Gyroid Ni/Al_2O_3 Catalyst for Enhanced CO_2 Methanation

Kedar Jivrakh[1,2], Ayesha Alkhoori[2,3], Kyriaki Polychronopoulou[2,3], Rashid Abu Al-Rub[3,4], Georgios N. Karanikolos[1,2,5*]

[1]*Chemical Engineering Department, Khalifa University, Abu Dhabi, UAE*
[2]*Center for Catalysis and Separations (CeCaS), Khalifa University, Abu Dhabi, UAE*
[3]*Mechanical Engineering Department, Khalifa University, Abu Dhabi, UAE*
[4]*Advanced Digital and Additive Manufacturing (ADAM) Center, Abu Dhabi, UAE*

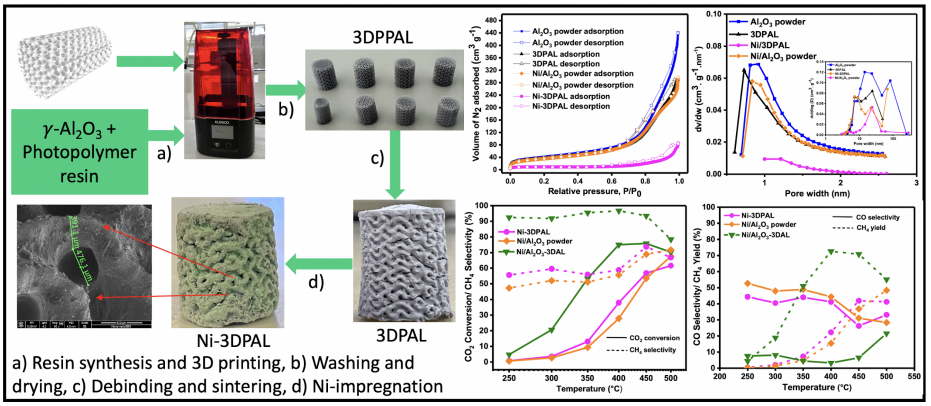
[5]*Department of Chemical Engineering, University of Patras, Patras, Greece*
[*]*Corresponding Author's E-mail address: georgios.karanikolos@ku.ac.ae*

Keywords: 3D printing, Gyroid, Methanation, CO_2 conversion

Introduction: The utilization of 3D printing in catalyst production for CO_2 methanation has emerged as a response due to the challenges posed by the highly exothermic reaction and high gas space velocity. These conditions necessitate enhancedmore efficient heat and mass transfer,, while maintaining optimal catalytic performance. In this study, we developed a 3D-printed a Ni/Al_2O_3 catalyst and evaluated its effectiveness for CO_2 methanation at various temperatures.

Experimental/methodology: To synthesize Printable Al_2O_3 resin, a carefully optimized blend of the latter commercial photopolymer resin and Al_2O_3 was prepared. The resulting resin was then employed to 3D print cylindrical gyroid sheet lattices, characterized by aa high surface area to volume ratio. Elegoo's Mars 3 Pro printer (3DPPAL) was utilized for this purpose. Subsequently, the printed samples were subjected to controlled heating in a furnace to facilitate debinding and the removal of photopolymer. They were then sintered at 650°C (3DPAL). In order to achieve the desired loading, the 3DPAL sample was impregnated with Nickel (Ni) using the wet impregnation technique [1]. For comparison purposes, Ni/Al_2O_3 powder with identical loading was also prepared, for comparison and the powder was also coated onto 3D-printed aluminium (Ni/Al_2O_3-3DAL) for comparison. Both the powder and printed catalysts underwent BET analysis, SEM-EDX, H_2-TPR, CO_2-TPD, and CO_2 methanation tests.

Results and discussion: The higher sintering temperature was seen observed to cause a further reduction in the surface area of Ni-3DPAL. To optimize further the process, it is recommended to increase the sintering temperature can be increased to remove the to eliminate any residual polymer, and raise the Ni loading in both the powder and printed samples can be increased. Comparatively, Ni/Al_2O_3-3DAL exhibited higher CH_4 selectivity, CH_4 yield, and CO_2 conversion than /Al_2O_3-3DAL Ni/Al_2O_3 powder and Ni-3DAPL. This was attributed to the apparent occurrence of reverse water gas shift in the latter. A reduction in surface area was observed in 3DPAL as compared to Al_2O_3 powder Notably, the CO yield was also the lowest for Ni/Al_2O_3-3DAL. The higher sintering temperature was seen to further reduce the surface area It is proposed that the improved activity is attributed to Enhanced heat dissipation due toresulting from the metal support utilized.is proposed to be responsible for the improvement in activity. After Ni loading, the surface area decreased further, as seen from the liquid nitrogen adsorption isotherms.



a) Resin synthesis and 3D printing, b) Washing and drying, c) Debinding and sintering, d) Ni-impregnation

Acknowledgments
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Understanding Titania Crystallization to Generate Engineered Anatase Particle Architecture

A. Jain[1], M. Kumar[1*]

[1]*Indian Institute of Technology Delhi, New Delhi, India*
[*]*manjeshkumar@chemical.iitd.ac.in*

Keywords: Catalysis, Crystal growth, Nonclassical mechanism, Growth modifiers

Introduction. Modulating the crystal shape and size with desirable exposed/terminating reactive facets is significant for fundamental studies and various technological applications [1]. Anatase phase of TiO_2 has been widely studied due to its extensive industrial applications [2], [3]. Here we present a novel, economically feasible and simplistic wet chemistry approach to synthesize titania crystals with high index facets with particle size control over 3 orders of magnitude (5 nm-3000 nm).

Experimental/methodology. The synthesis of titania particles was carried out using a hydrothermal method. Titanium Isopropoxide (TTIP) was mixed with alkyl ammonium hydroxide and DI water in stoichiometric ratio. Subsequently, the pH of the growth solution was adjusted in the range of 3-11 using various protic acids. The pH adjusted growth solution and pH adjusted solutions with modifiers (organic and inorganic) were subjected to hydrothermal treatment at 200 ˚C for 12h in dynamic conditions.

Results and discussion. In this study, we conducted the comprehensive investigations generating the crystals from a few nanometers to few microns with varied surface architecture and varied dimensionality (0-3 Dimensions) via modulation of physicochemical growth conditions. Unique structures generated here such as coral -shaped structure (Figure 1B and P4) provide high surface area while faceted crystals (Figure 1D and P2) formed serve as host for active metal sites. Further, we have also explored the crystallization pathways of anatase crystals, which shows that growth solutions with similar initial precursor phase traverse 4 different paths to generate these structures (shown in Figure 1). We observed different precursor phases such as nanosheets (Figure 1 P1), partially ordered domain (Figure 1 P2), rod-shaped microcrystalline (Figure1A), needle-shaped crystallite (Figure 1 P4), among others that generate an array of bulk crystals. These uncontrolled pathways were intervened using modifiers (organic molecules and inorganic salts) to generate more desired faceted crystals. Complete blueprint will be presented for rational design of titania crystals.

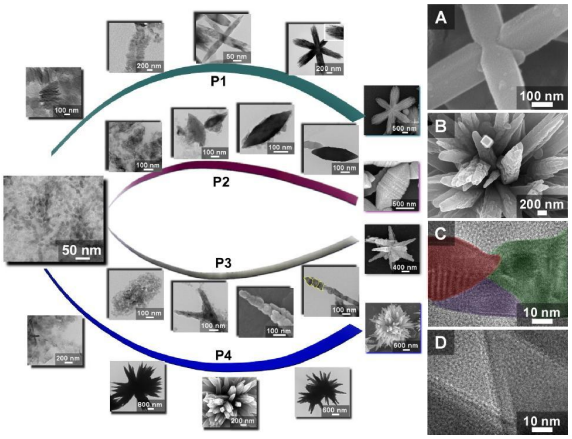

Figure 1| Palette of Anatase Crystallization. P1. The first curved path (green) represents formation of flower-shaped titania particle at high pH. All the paths show time-elapsed data from 0 min to 12h of hydrothermal treatment. P2. Represents the formation of a faceted particle at high pH using salt as modifier. P3. Shows the formation of highly branched star-like agglomerate at high pH using a different salt as modifier. P4. Shows the formation of coral-shaped titania particle at low pH. A. Cojoined rods at medium pH. B. Needle-like particle obtained at low pH. C. Oriented attachment of particle using modifier. D. faceted particle obtained using modifier

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Polypropylene imine (PPI) dendrimers as promising matrices for the immobilization of catalysts for hydrogen isotope exchange reactions

L. Jedlovčnik,[1] J. Höfferle,[1] J. Košmrlj,[1] V. Derdau,[2] R. D. Jansen-van Vuuren[1*]

[1]*University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, 1001 Ljubljana, Slovenia*

[2] *Research & Development, Integrated Drug Discovery, Isotope Chemistry, Sanofi-Aventis Deutschland GmbH, Industriepark Höchst G876, Frankfurt/Main 65926, Germany*

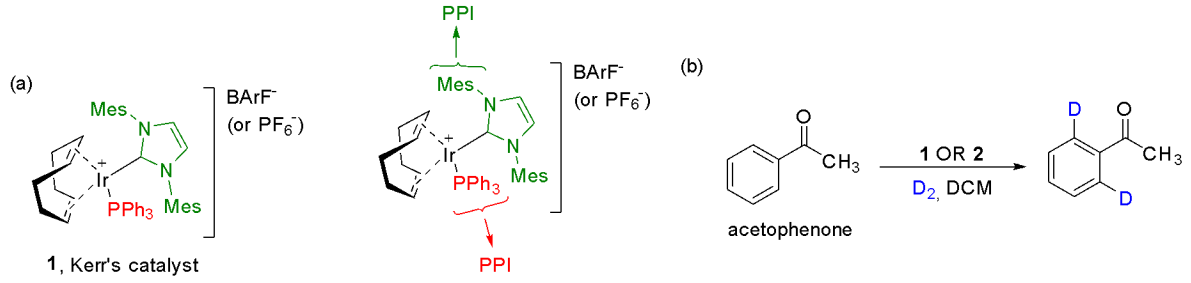
[*]*Ross.JansenvanVuuren@fkkt.uni-lj.si*

Keywords: recyclable, catalyst, deuterium-labelling, circular, immobilization, isotope exchange.

Introduction. Deuterium-labelled organic compounds are used in many applications.[1-4] The preparation of such compounds relies on catalysts such as bio-, organometallic or organo- catalysts. These catalysts are typically made using lengthy and expensive procedures. Some contain precious metals (e.g., Ir, Pd).[5] Furthermore, they are frequently used in a linear 'make-use-dispose' approach. The use of recyclable forms of these catalysts represents an advance towards circular chemistry,[6] and various strategies have been explored for the development of recyclable catalysts for the synthesis of deuterium-labelled organic compounds.[7-9]

Experimental/methodology. One approach to creating a recyclable catalyst involves immobilization of the parent catalyst on a polymer-based support. In this presentation, I will report on the design and synthesis of recyclable catalysts featuring a stimuli-responsive polypropylene imine (PPI) dendrimer matrix functionalized with reactive iridium-N-heterocyclic carbene centers (Kerr's catalyst, **1**), scheme, part (a). I will also present a comparison between the activity of the immobilized catalyst (**2**) *versus* the parent catalyst (**1**). Finally, I will discuss approaches taken for the recovery and reuse of the dendrimer catalysts.

Results and discussion. I will present evidence for the formation of the dendrimer-based catalysts and the effectiveness of their recovery and reuse. I will also highlight preliminary results obtained when comparing the activity of the dendrimer catalysts *versus* the parent catalyst in the deuterium-labelling of acetophenone, a simple model organic substrate, part (b), below.



1, Kerr's catalyst

2, Kerr's catalyst, immobilized on PPI either via the PPh_3 or the NHC group

Acknowledgments

dr. Damijana Urankar for HRMS analysis

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Emergence of active and stable platinum nanoparticles from titanate perovskites for catalytic applications

Y. Jeon[1,2], M. Kothari[2], D. N. Miller[2], A. Eva Pascui[3], J. Kilmartin[3], S. Ramos[4], A. Chadwick[4], J. T. S. Irvine[2*]

[1]*Department of Environmental and Energy Engineering, Yonsei University, Seoul, South Korea.*
[2]*School of Chemistry, University of St Andrews, St Andrews, UK.*
[3]*Johnson Matthey Technology Centre, Sonning Common, Reading, RG4 9NH, U.K.*
[4]*School of Physical Sciences, Ingram Building, University of Kent, Canterbury, CT2 7NH, U.K.*
[*]*jtsi@st-andrews.ac.uk*

Keywords: Platinum, Perovskite, Emergent nanoparticles, Catalytic applications

Introduction.
Platinum catalysts demonstrate exceptional ability in many important fields, e.g. in removing atmospheric pollutants. Typically, these are dispersed on a porous support, such as γ-Al_2O_3, with low loading of 0.5−2.0 wt% and have been extensively used in ECT (Emission control technology) applications [1,2]. However, it is expensive and not always sufficiently durable, due to Pt agglomeration and even sublimation at high temperature operation [3,4]. Here, we present a perovskite system in which 0.5 wt% of Pt is integrated into the support, and its subsequent conversion through exsolution to achieve a resilient catalyst.

Experimental/methodology.
Due to the instability of most Pt oxides at high temperature, a thermally stable platinum oxide precursor, Barium Platinate, is utilised to preserve the platinum as an oxide through the solid-state synthesis in an approach inspired by the Trojan horse legend [5].

Results and discussion.
A uniform equilibrated structure with active emergent Pt nanoparticles strongly embedded at the perovskite surface (Figure 1) was produced. The nanoparticles were also controllable in size and distribution by optimizing the procedure, yielding modified performance in CO oxidation activity with greatly improved stability [5]. This catalysts were further evaluated under a variety of reactions under realistic test environments, for example, Diesel Oxidation Catalysis.

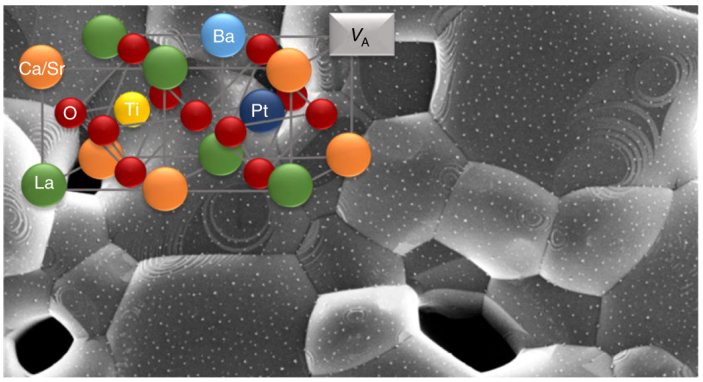

Figure 1 Emergent platinum nanoparticles on titanate perovskites

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SiO_2@Ni@ZrO_2 core-shell catalyst for combined steam and dry reforming of methane

Seorin Ji[1], Eun Jun Lee[1], Hyoseong Woo[1], Kwan-Young Lee[1*]

[1]*Department of Chemical and Biological Engineering, Korea University, 145 Anam-ro, Sungbuk-ku Seoul 02841, Republic of Korea*

[*]*Corresponding author (kylee@korea.ac.kr)*

Keywords: core-shell, combined steam and dry reforming of methane

Introduction. Hydrogen Energy is an alternative energy sources which is capable of large-scale, long-term storage and can be produced by various types of energe resources. Reforming of methane is a process that can produce hydrogen from methane, and this process is most widely used in industry. Recently, combined steam and dry reforming of methane (CSDRM) attracts much attention among various methane reforming. CSDRM is a combination of steam reforming of methane (SRM) and dry reforming of methane (DRM), and it produces hydrogen and carbon monoxide by using methane, carbon dioxide, and water. It has advantages that it consumes two main green house gases (CO_2, CH_4), and it exhibits higher coke resistance than DRM. Additionally, CSDRM produces syngas with H_2/CO ratio of 2, which has advantages in sequential processes such as Fisher-Tropsch synthesis.

In CSDRM, Ni based catalyst is most widely used for its high activity and reasonable price. However, it has serious problem in metal sintering and coke deposition compared to noble metal based catalyst. Catalyst with core-shell structure can prevent catalyst deactivation by physically suppressing metal sintering and inhibiting coke deposition [1,2]. So, we suggest core-shell SiO_2@Ni@ZrO_2 catalyst for the long-term stability of CSDRM.

Experimental/methodology. Ni nanoparticle was synthesized by ammonia-Borane Hydrolysis. SiO_2 was synthesized by modified stöber method. Ni nanoparticle and SiO_2 were mixed in room temperature with hexane overnight to form Ni@SiO_2 sphere. ZrO_2 shell was formed above the sphere using zirconium butoxide solution.

Ni/SiO_2 was synthesized by incipient wetness impregnation method as a reference catalyst.

CSDRM reaction was conducted using a tubular quartz fixed bed reactor at 800 °C, atmospheric pressure to examine catalyst activity. Catalysts were reduced at 500 °C for 3 hours in 10% H_2/N_2 gas mixture with flow rate of 100 mL/min before reaction. Feed gas mixture consisted of CH_4, CO_2, H_2O, N_2 in a molar ratio of 10:4:8:78 with flow rate of 100 mL/min.

Results and discussion. In XRD, it is confirmed that highly dispersed Ni was formed through the crystal structure of Ni/SiO_2 and SiO_2@Ni@ZrO_2. Also, SiO_2@Ni@ZrO_2 formed a core-shell structure through TEM and EDS mapping. ZrO_2 shell structure was estimated to prevent sintering of Ni nanoparticles.

As a result of comparing the CSDRM activity at 800 °C, the SiO_2@Ni@ZrO_2 catalyst showed higher activity and stability than Ni/SiO_2. The SiO_2@Ni@ZrO_2 catalyst maintained constant CH_4 and CO_2 conversion for more than 30 hours, meanwhile, CH_4 conversion and CO_2 conversion of Ni/SiO_2 have significantly decreased for 30 hours. In addition, various catalyst characterization analysis was performed to identify the cause of higher activity and stability of SiO_2@Ni@ZrO_2 than that of Ni/SiO_2. As a result, we suggest that core-shell structure of SiO_2@Ni@ZrO_2 improved its stability in long-term reaction.

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Atomic-Layer-Deposition Derived Pt sub-nano Clusters on the (110) Facet of Hexagonal Al_2O_3 Plates: Efficient for Formic Acid Decomposition and Water Gas Shift

T.T. Chen[1], J.T. Chen[2], W. J. Song[1], Shihao Hu[1], X.Z. Feng[1], Z.X. Chen[1], W.J. Ji[1]

[1] *Key Laboratory of Mesoscopic Chemistry, MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China*

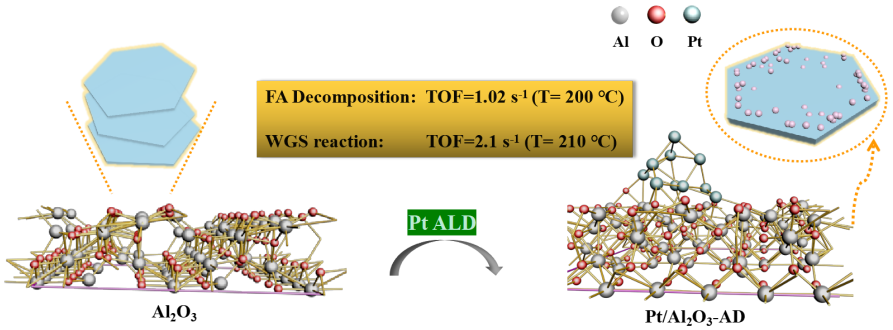
[2] *University of Toronto, Toronto, Ontario M5S1A1, Canada*

**jiwj@nju.edu.cn*

Introduction. Considerable efforts have been devoted to the kind of renewable energy.[1] Hydrogen is regarded as a green energy carrier and a key to achieve low-carbon energy economy. [2] Formic acid (FA) has been recognized as one of the promising hydrogen carriers due to its high energy density (1.22 g/cm^3). The water gas shift (WGS) is another critical process to increase hydrogen production. It is well known that the size of metal entities can considerably determine catalyst activity. In application of noble metal catalysts, how to improve utilization efficiency of noble metals meanwhile to enhance catalyst efficiency is always a hot topic in the field of catalysis [3,4].

Experimental/methodology. Our catalysts were designed and fabricated according to the following tatics: first, the ion liquid-assisted synthesis of alumina is conducted to obtain regularly shaped hexagonal Al_2O_3 plates, so that the majority of desirable (110) facet is exposed; secondly, the Pt nano-clusters ranging from ca. 0.58 nm to 0.74 nm and 1.20 nm are preciously deposited onto the (110) facet of alumina support through the atomic-layer-deposition approach. The Pt clusters were also deposited on the polycrystalline Al_2O_3 for comparison. DFT simulations, characterizations, and activity evaluations were conducted to explicate the role and significance of the unique metal-oxide interfacial structure for the target reactions.

Results and discussion. We have precisely deposited the size-tunable Pt clusters onto the Al_2O_3 (110) facet and Al_2O_3 rods through atomic-layer-deposition strategy as well as deposition-precipitation method. The resulting materials were applied for WGS and FA decomposition. Compared to the Pt nanoparticles on the Al_2O_3 (110) facet or Pt fine clusters on the polycrystalline rod-like Al_2O_3, those ultrafine Pt clusters on the Al_2O_3 (110) facet with very low Pt loading (0.07wt%) exhibit exceptional low-temperature CO conversion for WGS, with a TOF_{CO} of 2.1 s^{-1} at 210℃ and a CO conversion rate of 10.2 mmol g_{Pt}^{-1} s^{-1}, 4.7, 7.7, and 9.7 times higher than that on 0.34%Pt/Al_2O_3-AD, 0.56%Pt/Al_2O_3-AD and 0.46%Pt/Al_2O_3-DP. The current 0.07%Pt/Al_2O_3-AD catalyst also outperforms the Pt/Ir-based single atom catalysts. For FA decomposition, 0.07%Pt/Al_2O_3-AD affords the highest TOF of 1.02 s^{-1} at 200℃ with almost full FA conversion, and the H_2 formation rate is 4.5 times higher than that obtained on 0.46%Pt/Al_2O_3-DP. The unique synergism involved between the ultrafine Pt entity and the specific (110) facet of Al_2O_3 brings about significant modification in electron state and local geometry of Pt atoms in the ultrafine Pt clusters which are further supported by the DFT simulations, accounting for the superior performances in both FA decomposition and WGS.



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Novel Oxyhydride Electride Activating Co Catalyst for Ammonia Synthesis

Yihao Jiang[1], Masayoshi Miyazaki[1], Hideo Hosono[1], Masaaki Kitano[1,*]

[1] *International Research Frontiers Initiative MDX Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*
[*] *kitano.m.aa@m.titech.ac.jp*

Keywords: Oxyhydride, Electride, Ammonia synthesis, Catalysts

Introduction.

Ammonia is one of the most important chemicals due to its broad application in industrial production. Co is studied as a practical catalyst for ammonia synthesis to replace noble metal Ru. However, the weak Co−N interaction makes Co inactive for ammonia synthesis using conventional supports especially under mild reaction conditions.[1] Previous research demonstrates that hydride materials like LiH and BaH_2 are very effective supports for Co-based catalysts.[2,3] However, the reported hydride-based catalysts are very sensitive toward air and readily deactivated due to the irreversible decomposition by the reaction with ambient atmosphere. Therefore, the major challenge of catalyst design for green ammonia synthesis is to be Ru-free with high catalytic performance and chemically-robust. Here, we report a novel oxyhydride electride material $BaAl_2O_{4-x}H_y$ as an efficient and chemically-durable support for Co catalyst in ammonia synthesis.

Experimental/methodology.

$BaAl_2O_{4-x}H_y$ was synthesized by solid-state reaction of γ-Al_2O_3, BaH_2 and $BaCO_3$ mixed in an agate mortar under H_2 gas flow. $BaAl_2O_{4-x}H_y$ and $Co_2(CO)_8$ were physically mixed and heated at 500°C under N_2/H_2 mixed gas flow to load Co. The ammonia synthesis reaction was evaluated using a fixed-bed flow reactor.

Results and discussion.

$BaAl_2O_{4-x}H_y$ has a stuffed tridymite structure that provides interstitial cage sites (Figure 1) to accommodate anionic electrons and H^- ions. The existence of anionic electrons is confirmed by iodometric titration and magnetic susceptibility measurements, and H^- ions are confirmed by TPD and DRFTIR measurements. DFT calculations reveal that the interstitial cage sites play a pivotal role to stabilize anionic electrons or H^- ions. Co-loaded $BaAl_2O_{4-x}H_y$ achieved significant activity (500 mmol g_{Co}^{-1} h^{-1}) under mild conditions (340°C, 0.90 MPa) with a very low apparent activation energy (49.6 kJ mol^{-1}), which is in complete contrast to the catalytic performance of $Co/BaAl_2O_4$ (0.7 mmol g_{Co}^{-1} h^{-1}, 100 kJ mol^{-1}). Isotope N_2 exchange reaction experiments reveal that the energy barrier of N_2 cleavage is largely lowered due to the strong electron donation. Furthermore, the lattice H^- ions further boost ammonia synthesis by accelerating the N−H bond formation. These properties make this catalyst even comparable to the latest Ru catalysts at 300°C. Most importantly, even after air exposure, the activity of $Co/BaAl_2O_{4-x}H_y$ could be recovered by simple annealing in H_2/N_2 flow. This is because the three-dimensional AlO_4-based network in the stuffed tridymite structure has strong chemical stability and protects anionic electrons and H^- ions from the oxidation. Such robustness and reusability are distinct advantages over the reported hydride-based Co catalysts for ammonia synthesis.

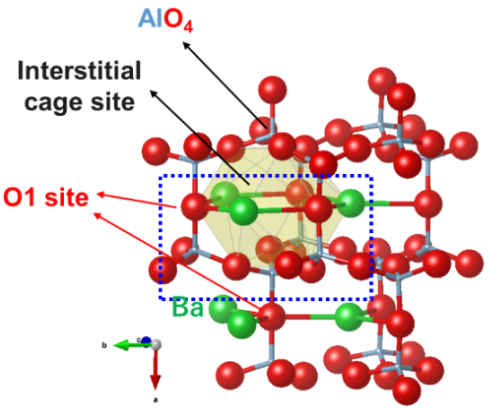

Figure 1. Crystal structure of $BaAl_2O_4$ with stuffed tridymite structure.

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Plasma jet sputtering as a perspective tool for preparation of Co-Cu-Mn oxides: effect of preparation conditions on properties and oxidation activity

K. Jirátová[1*], M. Čada[2], R. Perekrestov[2], J. Balabánová[1], M. Koštejn[1], J. Maixner[3], P. Topka[1], Z. Hubička[2], F. Kovanda[4]

[1]*Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, Prague, Czech Republic*

[2]*Institute of Physics of the Czech Academy of Sciences, Prague, Czech Republic*

[3]*Central Laboratories, University of Chemistry and Technolgy, Prague, Czech Republic*

[4]*University of Chemistry and Technology, Prague, Czech Republic*

[*]*jiratova@icpf.cas.cz*

Keywords: plasma sputtering, metal oxides, oxidation of ethanol

Introduction. The alternative deposition method based on sputtering of metal nozzle (hollow cathode) with a flowing gas has attracted much attention. Inside the nozzle, a very intense discharge is ignited and the working gas (usually argon) flowing into a vacuum chamber forms the so-called plasma jet [1]. We decided to study a Co-Cu-Mn oxide system from the point of view of various conditions of plasma jet sputtering on stainless steel meshes and reveal their influence on the properties and activity in the total oxidation of ethanol as a model compound of VOCs.

Experimental/methodology. The Co, Cu, and Mn were deposited on stainless steel meshes (circular meshes with an outer diameter of 25 mm) by sputtering a) from three hollow cathodes in argon, b) from three hollow cathodes in argon and oxygen, and c) using hollow cathode prepared from calcined Co-Cu-Mn hydroxycarbonate pellets. After deposition, all samples were calcined for 4 h at 500 °C in air. The properties and catalytic activity were compared with those of Co, Ni-Co, and Ni-Cu oxide catalysts prepared on meshes using hollow cathode (or radio frequency magnetron) sputtering. The catalytic performance (on a per gram oxides basis) was compared with that of a pelletized commercial Co-Mn-Al catalyst (Astin 2-100).

Results and discussion. The experimental data of ethanol oxidation showed that the Co catalyst prepared by RF magnetron sputtering with argon as the working gas on stainless steel meshes was the least active of all catalysts. The use of a hollow Co cathode and the presence of oxygen in the working gas increased the performance significantly (almost 5 times). The activity of the binary catalytic components, Ni-Co [4] and Ni-Cu [5] oxides with a molar ratio of Ni:X (X=Co or Cu) of 1:1 obtained with hollow cathodes made of corresponding NiCo and NiCu alloys in Ar and oxygen environment did not cause an increase in the oxidation activity of the catalysts. The Co-Cu-Mn catalyst sputtered from three hollow cathodes using Ar as working gas showed comparable activity to the Co catalyst prepared in $Ar+O_2$ environment. The presence of oxygen in the working gas during simultaneous plasma jet sputtering of Co, Cu, and Mn was again reflected in the increased activity of the catalyst. Due to the different deposition rates of Co, Cu and Mn, we investigated the possibility of using as a hollow cathode a calcined Co-Cu-Mn hydroxycarbonate of defined composition with a molar ratio of Co:Cu:Mn of 3:1:1. Even in an $Ar+O_2$ environment, the activity of the catalyst obtained in this way was the lowest among the Co-Cu-Mn oxide catalysts studied (which could probably be due to the higher Cu content at the expense of Co). A significant advantage of thin-film catalysts supported on stainless steel meshes is (i) the very low amount of the expensive active phase required for catalyst preparation and (ii) low pressure drop across the catalyst bed. Due to the effect of internal diffusion during the catalytic reaction, the sputtered catalysts were up to 26 times more active than commercial pelletized Co-Mn-Al catalyst, although the amount of metal oxides in catalyst bed was 563 times lower.

Acknowledgments

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Mesoporous Pt–MnO_x–Al_2O_3 catalyst for dehydrogenation of perhydro benzyltoluene: Highly dispersed Pt–MnO_x clusters for activity boosting

Yeongin Jo, Young-Woong Suh*
Department of Chemical Engineering, Hanyang University, Seoul 04763 (Republic of Korea)
**E-mail: ywsuh@hanyang.ac.kr*

Keywords: LOHC, dehydrogenation, catalyst, surface mobility

Introduction. To overcome thermodynamic hurdles in the dehydrogenation reaction, which is considered as the bottleneck of LOHC technology, we recently proposed a mesoporous Pt–Al_2O_3 catalyst synthesized by SDP (solvent-deficient precipitation) method [1]. Remarkably, this catalyst showed a much higher ratio of Pt single atoms and clusters compared to conventional catalysts. Herein, this consequence has been investigated in the respect of support properties and then is extended to the preparation of a new mesoporous Pt–MnO_x–Al_2O_3 catalyst (mPtMnA) to surpass the mesoporous 1 wt.% Pt–Al_2O_3 catalyst composed of Pt single atoms exhibiting rather low activity in the dehydrogenation of perhydro benzyltoluene (H_{12}-BT). To maximize the interaction between Pt and MnO_x, we optimized the construction process from Pt atoms to Pt–MnO_x clusters by tuning the mobility of Pt single atoms on the surface of Al_2O_3.

Experimental/methodology. The applied SDP method is a one-pot synthesis to use the active metal source of $(NH_3)_4Pt(NO_3)_2$ and add $Mn(NO_3)_2{\cdot}6H_2O$ as Mn source. After grinding, the gel-phase precursor was subjected to the following heat treatment: calcination at 600 °C for 5 h with a ramping rate of 2 °C min^{-1} and H_2 reduction at 500 °C for 3 h with different ramping rates. The prepared catalysts are denoted as mPt*x*MnA. The content of Pt is fixed at 1 wt.%, and *x* is the molar ratio of Mn to Pt.

Results and discussion. Compared with other synthesis methods, the synthesized mPtMnA exhibited the higher activities, possibly because of strong interaction between Pt and MnO_x. In particular, the dehydrogenation performance was greatly improved at the Mn/Pt mole ratio of 0.33 (Fig. 1a). To strengthen Pt–MnO_x interaction, the ramping rate in H_2 reduction was controlled, thereby, highly dispersed Pt–MnO_x composite cluster could be created, affording superior dehydrogenation performance (Fig. 1b). The SDP-derived pure Al_2O_3 was reported to have defect sites similar to those of boehmite [2], which can explain the high dispersion of Pt in the mPtA. Thus, it active Pt atoms are believed to have surface mobility due to unstable Al_2O_3 sites. The uniqueness of mPtA likely originates from the defective structure of Al_2O_3, which is also effective in the mPtMnA catalyst. From the HAADF-STEM images and CO-DRIFTS results, we can conclude that highly dispersed Pt–MnO_x clusters with a size of 1.3 nm are formed from Pt single atoms anchored in the unstable sites at high ramping rates.

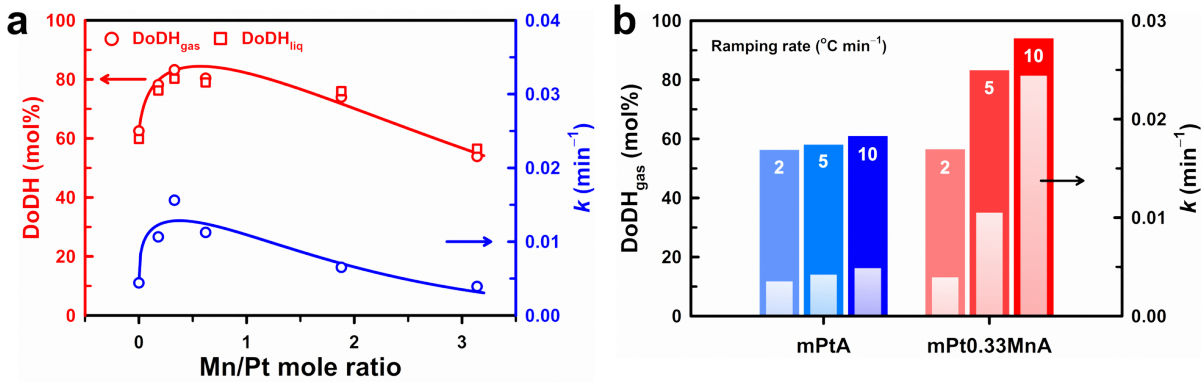

Figure 1. DoDH and *k* plotted against (a) the Mn/Pt mole ratio and (b) the ramping rate in the reduction process. $DoDH_{gas}$ (filled bars) and initial rate constant *k* (blank bars).

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Preparation and characterization of promoted supported MoS_2 catalysts for hydrodenitrogenation

J.Kattelus[1*], J.Velasco[1], P.Auvinen[1], S.Albersberger[2],
H.Jiang[1], K.Meinander[1], A.Chahal[1], R.Karinen[1], R.L.Puurunen[1]
[1]*Aalto University, Department of Chemical and Metallurgical Engineering, Espoo, Finland*
[2]*Neste Oyj, Jalostamontie 36, 06850 Porvoo, Finland*
[*]*joakim.kattelus@aalto.fi*

Keywords: renewable fuels, hydrodenitrogenation, MoS_2, incipient wetness impregnation

Introduction. Catalytic hydrodenitrogenation (HDN) is widely used for removing nitrogen-containing impurities from petroleum [1, 2]. The most commonly used HDN catalysts are MoS_2 supported on alumina and promoted by Ni [1, 2]. Alternative renewable feedstocks contain significantly higher amounts of nitrogen [3], which means replacing fossil feedstocks requires the development of new, highly active catalysts for the HDN process [2]. In this work, we present an initial study on the preparation of alumina-supported MoS_2-catalysts incorporating Ni, Na, Cr, Pt or Ru as promoters. The goal was to investigate and compare the effect these promoters have on the structure of the MoS_2 phase.

Experimental/methodology. Oxidic catalyst precursors were prepared using incipient wetness co-impregnation followed by calcination at 500 °C for 120 min under a 100 ml/min flow of air. Prior to impregnation, the γ-Al_2O_3 support had been calcined at 500 °C for 300 min . Ammonium heptamolybdate hexahydrate (AHM), nickel(II) nitrate tetrahydrate, sodium nitrate, chromium(III) nitrate, platinum(IV) nitrate and ruthenium nitrosyl nitrate were used as precursors. Citric acid was used as an additive, since previous work had shown it prevented the formation of crystalline MoO_3, thus improving the dispersions and metal loadings of the obtained catalyst precursors. The oxidic catalyst precursors were transformed into sulfide catalysts by sulfidation for 120 min at 400 °C in 10 vol% H_2S/H_2 in a batch reactor. In addition to the promoted catalysts, an unpromoted reference catalyst was also prepared with the same method.

Both oxidic catalyst precursors and sulfided catalysts were characterized. Powder X-ray diffraction (XRD), X-ray fluorescence (XRF), inductively coupled optical emission spectroscopy (ICP-OES), N_2 physisorption and Raman spectroscopy were used in order understand the physicochemical properties of the calcined catalyst precursors. Sulfided catalysts were analyzed using XRD, ICP-OES, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) combined with energy-dispersive X-ray spectroscopy (EDS).

Results and discussion. Co-impregnation followed by calcination was found to give oxidic catalyst precursors in which the Mo and Ni, Na, Cr and Pt species were well dispersed on the support. However, crystalline RuO_2 was formed on the $RuMo/Al_2O_3$ oxidic precursor, implying that Ru dispersion was poor.

Sulfidation of the catalyst precursors was found to give the expected MoS_2 phase, but the nature of the promoter species after sulfidation varied. XPS showed evidence for the formation of the mixed NiMoS phase, which is generally accepted to be highly active for HDN. In contrast, it was deemed likely that Na remained oxidic after sulfidation. The other promoter metals Cr, Ru and Pt were reduced during sulfidation, which was deemed undesireable, since reduced metals are likely poisoned by H_2S and therefore unlikely to significantly improve the HDN activity.

Even though no evidence was found for the formation of a mixed promoter-MoS_2 phase with any of the tested promoters except Ni, analysis of TEM images showed that the height of the MoS_2 stacks was lower for all the promoted catalysts, compared to the unpromoted reference catalyst. Thus, it was concluded that the promoters had an effect on the morphology of the MoS_2 phase and that less reducing sulfidation conditions should be tested in future work, in order to convert Cr, Pt and Ru into sulfidic phases.

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Selective Hydrogenation of Acetylene in Excess of Ethylene over Pd nanoclusters in 3D graphene-like carbon catalysts

D. Kaucký[1,*], J. Morávková[1], R. Pilař[1], G. Sádovská[1], S.S. Faal-Rastegar[1], A. Vondrová[1], P. Sazama[1]

[1] *J. Heyrovský Institute of Physical Chemistry of the AS ČR, Dolejškova 2155/3, Prague, the Czech Republic*
[*]*Corresponding Author: dalibor.kaucky@jh-inst.cas.cz*

Keywords: Acetylene, Ethylene, Selective Hydrogenation, Palladium, Charcoal, nano-structured Carbon.

Introduction. Selective hydrogenation of acetylene in an excess of ethylene over Pd catalysts is important for the purification of ethylene for polymerization processes. This study analyses the effects of the Pd clusters morphology and the Pd clusters-supports electronic interaction on the selectivity to the individual products (Figure 1). We investigated the possibilities of using Pd clusters deposited on a 3D graphene-like organized structure of zeolite-templated carbon to modify the electronic properties of the Pd clusters and exploit the well-accessible surface of the 3D graphene-like material for the preparation of hydrogenation catalysts.

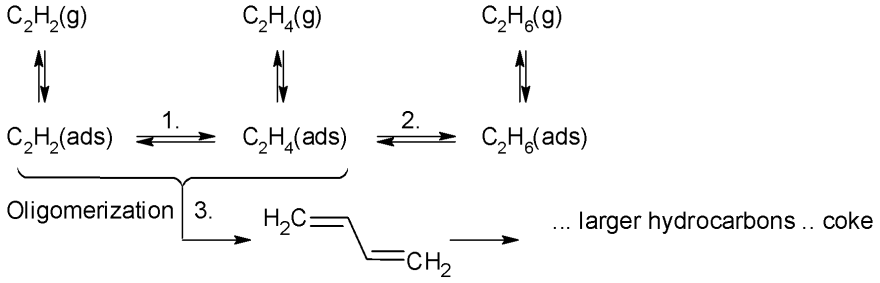

Figure 1. The reaction scheme: acetylene hydrogenated to ethylene, and/or over-hydrogenated to ethane, while unsaturated reactants could condensate to higher products.

Experimental/methodology. The well-defined and regular 3D channels system of the faujasite zeolite was replicated into the zeolite templated carbon material with well-defined dimensions and spatial connectivity of the micropores by nanocasting. In the process of zeolite nanocasting, carbon atoms were generated along the walls of the regular zeolite micropores. The faujasite zeolite of the molecular Si/Al ratios 6 in the H^+ form was used as a hard template. Carbonization of the zeolite was performed using chemical vapour deposition with propylene as a carbon precursor. The subsequent selective removal of the structural lattice of the zeolite provided an ordered 3D microporous graphene-like Y-carbon material [1]. Pd/Y-carbon, Pd-alumina and Pd-silica catalysts were prepared by an impregnation method.

Results and discussion. The catalytic studies demonstrate that the electronic interactions of the Pd clusters with the graphene layer and the well-accessible surface of the 3D organized structure of Pd/Y-carbon provide significantly higher activity compared to traditional Pd catalysts while maintaining high selectivity for the preferential hydrogenation of the triple bond in acetylene. The approach enabled an adaption of the electronic properties and the dispersity of active Pd clusters to increase the reaction rates and to tailor the catalyst selectivity.

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Mechanochemical generation of acid surface sites at the interface TiO_2/graphite: application for the dehydration of formic acid

A. Guerrero-Ruiz[1], M. Yruela-Garrido[1], N. Martín-Rodríguez[1], E. Campos[1], J. M. Conesa[1], I. Rodríguez-Ramos[2], E. Castillejos[1]

[3]*Dto. de Química Inorgánica y Química Técnica, UNED, Madrid, Spain,* [2]*Instituto de Catálisis y Petroleoquímica (ICP-CSIC), Madrid, Spain,*

[*]*aguerrero@ccia.uned.es*

Keywords: formic acid, dehydration, TiO_2/graphite catalysts

Introduction. Mechanochemical methods have emerged as simple and effective synthesis routes for producing catalytic materials [1]. This synthetic strategy, typically based on reactive extrusion or ball milling, provides materials with unusual properties based on a large variety of ingredients: metals, metal oxides (including mixed oxides) or hybrid composites (involving zeolites, MOFs, COFs, etc.). When regarding carbonaceous materials as support of metal nanoparticles some examples have been described [2], but no studies with graphite or carbon materials have been reported for their interaction with metal oxides.

In the present communication, we describe the possible formation of new acid sites at the surface of TiO_2 when it is mechanically treated with a high surface area graphite. Furthermore, these catalytic materials have been evaluated in the formic acid (FA) dehydration reaction [3].

Experimental/methodology. Three composite materials, TiO_2-graphite, with weight percent of 25/75, 50/50 and 75/25 were prepared by a procedure consisting of a mechanical mixture of both solids, previously ground in an agate mortar, using ultrasounds under ethanol as inert solvent (4 cycles of 20 min.). The starting materials are both commercially available: TiO_2 (Degussa, S_{BET}= 46 m^2/g) and high surface area graphite (HSAG from Timca, S_{BET}= 300 m^2/g). Before FA reaction studies the samples were treated at 300 °C under N_2 gas. Catalytic tests were performed in a continuous flow reactor with a reactant feed of $5.4x10^{-3}$ mol FA/min. All materials were characterised by Thermogravimetric Analysis, CO_2-TPD, NH_3-TPD, XRD and XPS.

Results and discussion. Catalytic measurements (Figure 1.A) show an improvement of specific catalytic activity to produce carbon monoxide for all mixture catalysts compared with the bare TiO_2. It should be notice that these samples do not suffer significant deactivation, even at higher reaction temperatures (250 °C). XRD does not display signals of anatase to rutile transformations in the TiO_2 structures. NH_3-TPD (Figure 1.B) reveals that in the mixture materials, prepared by mechanochemical interaction between TiO_2 and HSAG, an extra amount of acidic surface sites is generated. If it is assumed that dehydration of FA to CO and H_2O occurs over acidic centers, these new acidic sites can explain the improved catalytic activities of the mixture materials. Finally, in the XPS analysis of the Ti_{2p} peaks a significant shift of binding energies is observed when comparing pure TiO_2 and mixture TiO_2-graphite composites. This could be interpreted as a transfer of electrons at the interface of both components [4], but further measurements are required to confirm this hypothesis.

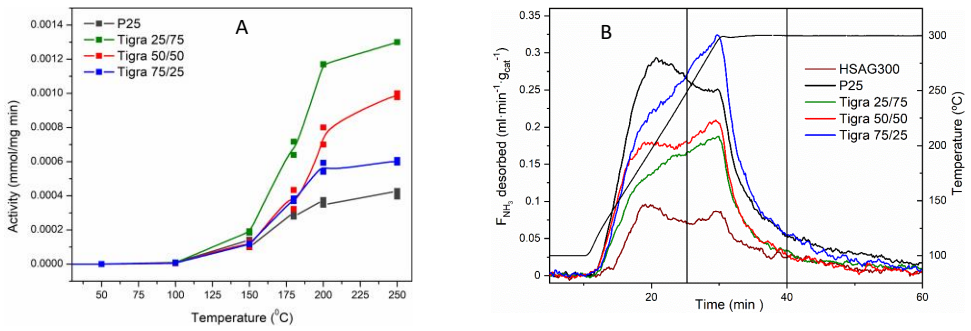

Figure 1. Comparative catalytic activities at different reaction temperatures for FA dehydration (A) and NH_3-TPDs (B).

Acknowledgments

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Supercritical Ion Exchange: A Novel Method for Cu-Zeolite Synthesis Enabling the Tuning of Active Sites Towards NH_3-SCR of NOx

T.B. Sari[1], H. Yousefzadeh[1], D. Sanlı[2], S.E. Bozbag[1], C. Erkey[1,*]

[1]*Department of Chemical and Biological Engineering, Koç University, Istanbul, Turkey,*

[2]*Ford Otosan R&D Center, Sancaktepe, 34885, Istanbul, Turkey,*

[*]*cerkey@ku.edu.tr*

Keywords: NH_3-SCR, NOx, Cu-zeolite, Supercritical fluids.

Introduction. Investigation of effects of synthesis method on catalyst performance is of high importance for the development of high performance diesel engine aftertreatment catalysts. Cu-zeolites, especially Cu-SSZ13 has been a center of attention as catalyst for Selective Catalytic Reduction of NOx. These catalysts are conventionally synthesized via aqueous ion exchange (AIE). Our group recently introduced the supercritical ion exchange (SCIE) route for Cu-zeolite synthesis and showed a certain degree of site speciation and auto-reduction differences among Cu sites formed by SCIE and AIE towards direct conversion of methane to methanol [1,2]. In this study, we extended the SCIE method to synthesize Cu-SSZ13 (CuS), Cu-ZSM5 (CuZ) and Cu-MOR (CuM) NH_3-SCR catalysts for the first time in literature and analyzed their performance.

Experimental/methodology. CuS (Si/Al:15), CuZ (Si/Al:23) and CuM (Si/Al:10) catalysts were synthesized via SCIE in supercritical CO_2 medium using copper(II)trifluoroacetylacetonate ($Cu(tfa)_2$). SCIE isotherms were measured at 40-80 °C and 28 MPa. CuM was also prepared via AIE using copper(II) acetate. Catalysts were characterized using XRD, FTIR, UV-Vis and XPS. Active species (ZCuOH or Z_2Cu [3]) were characterized via H_2-TPR, NO_2-TPD and NH_3-TPD. Performance analysis of catalysts were carried out in a bench-top reactor. Steady state NH_3 oxidation, NO oxidation and Standard SCR reactions were performed between 150 to 500°C at 100k h^{-1}. Intrinsic kinetic parameters (activation energy (Ea) and pre-exponential factor) of SCIE-CuS and CuZ for Standard NH_3-SCR of NO were obtained by running the reactor at differential conditions and assuming 1st order reaction. Feeds were 500 ppm NO and/or NH_3 or NO_2, 0-5% H_2O, 0-8%O_2 in N_2 balance.

Results and discussion. SCIE isotherms showed that Cu loading could easily be tuned by adjusting equilibrium Cu concentration and temperature during synthesis. After SCIE, FTIR band at 1301 cm^{-1} associated with v(C=C)+v(C-H) stretching vibrations in the $Cu(tfa)_2$ was observed of all CuM, CuZ, and CuS (Fig. 1a) with blue shifts of 4, 2, and 5 cm^{-1}, respectively, suggesting that some of the formed trifluoroacetylacetone, a product of the SCIE reaction [1], chemically bonded to the zeolite enabling site selective Cu exchange. In addition, H_2-TPR (Fig. 1b), NO_2-TPD and NH_3-TPD profiles showed that the structure and number of Cu species strongly depend on the SCIE conditions. To illustrate this, low temperature (150-200 °C) Standard SCR intrinsic kinetic parameters were measured and Z_2Cu site dominated CuS had a lower pre-exponential factor ($6.6*10^8$ $m^3/g_{cat}/s$) and lower Ea (64 kJ/mol) than ZCuOH dominated CuZ ($3.5*10^{11}$ $m^3/g_{cat}/s$ and 87 kJ/mol, respectively). This was also in line with very low NH_3 oxidation and NO oxidation performance of CuS and very high activity of CuZ towards these aforementioned reactions. With the purpose of comparing synthesis methods, Standard SCR activities of SCIE-CuM and AIE-CuM catalysts were measured. SCIE catalyst showed higher deNOx performance than AIE-CuM catalyst at both lower (<250 °C) and high temperature (>400 °C) with lower N_2O production at high temperatures (Fig. 1c). These results underline the significant potential of SCIE technique for the synthesis of NH_3-SCR catalysts for NOx abatement.

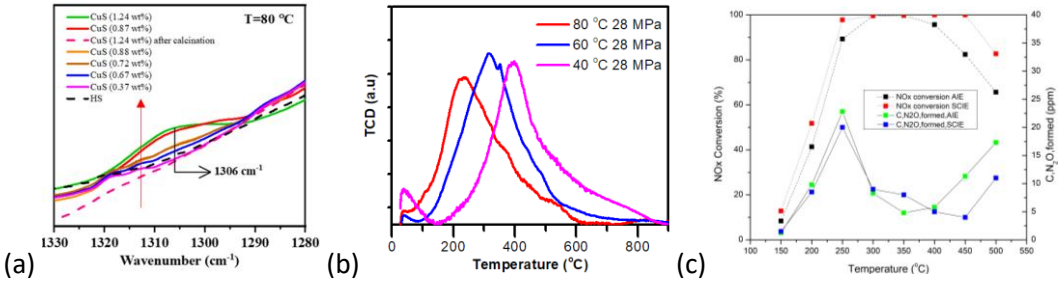

Figure 1 (a) FTIR spect.ra of various CuS before and after SCIE (b) H_2-TPR profiles of CuS (0.67 wt%) prepared via SCIE at different synthesis conditions (c) Standard SCR NO conversion differences of CuM prepared via SCIE and AIE (2 wt%).

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Catalysts and reactors under dynamic conditions for energy storage and conversion

Utilizing the redox cycability of modified spinel precursors for reactivation of Ni-based CO_2 methanation catalysts

Dennis Weber[1], Tanja Franken[1*]

[1] *Friedrich-Alexander-Universität Erlangen-Nürnberg, Institute of Chemical Reaction Engineering, Group of Catalytic and Electrocatalytic Systems and Processes, 91058 Erlangen, Germany*
[*] *tanja.franken@fau.de*

Keywords: Catalysis, CO_2 methanation, spinels, mixed metal oxides

Introduction. Nickel is widely used as catalytic active metal for the CO_2 methanation due to its high selectivity and low cost. For Ni/Al_2O_3 catalysts, sintering of the nickel particles on the surface leads to a decrease in catalytic activity with increasing time-on-stream, especially under dynamic H_2 dropout conditions.[1,2] Therefore, a catalyst is needed in which the nickel particles are both finely dispersed and stable. Spinels offers atomically distributed Ni, but their high stability makes its activation challenging. However, we demonstrate that spinel phases can be tailored to allow low temperature activation, creating finely dispered and highly active Ni sites, that are redox cycable to reverse potential deactivation.

Experimental/methodology. $Ni_{0.9}Mn_xAl_{2-x}O_4$ ($0 \leq x \leq 2$) catalysts were prepared by coprecipitation of the corresponding nitrates with one molar sodium hydroxide at a constant pH of 9 and concurrent calcination at 800°C. Catalytic experiments were performed in a fixed-bed reactor at ambient pressure.

Results and discussion. The Mn-tailored spinels have good low temperature reducibility and show higher activity and stability compared to supported catalyst. The methane yields achieved with the optimized spinel composition are on average about 45% higher than with the supported catalysts. No deactivation was observed for these spinel catalyst in both static and H_2 dropout experiments with a time-on-stream of over 100 h.[3] In addition, the redox reversibility of the spinel phase enables to reintegrate and redisperse the catalytically active nickel particles, reversing potential deactivation. This so-called concept of "Dynamic Responsive Methanation Catalysts" (cf. Figure 1A) is, with regard to the use of renewable energies for hydrogen production and the associated hydrogen dropouts, a possibility to utilize these dynamic operating conditions for reactivation of the catalyst. The spinel catalyst shows high redox cycability, with activity and selectivity remaining nearly constant after 5 consecutive cycles of active site formation by reduction and active site reintegration by oxidation into the hosting spinel structure (c.f. figure 1 B & C).

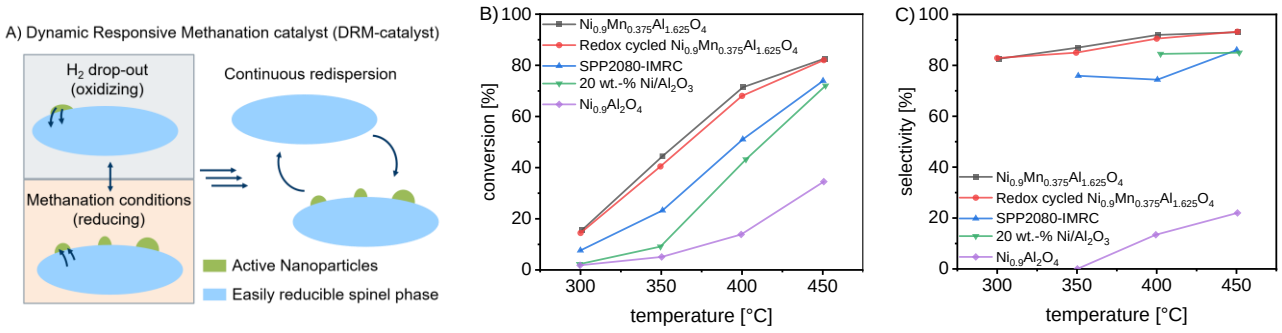

Figure 1: Performance of activated Ni based catalyst precursor in the methanation of CO_2 to methane. A) Dynamic Responsive Methanation Catalysts concept B) CO_2 conversion, C) CH_4 selectivity. Activation conditions: 10% H_2 in Ar 450 °C 60 min, methanation conditions: c(CO_2) = 6,25 vol%, CO_2/H_2 = 1/7.5 diluted in Ar, GHSV = 20000 h^{-1}, WHSV = 10.5 mln/(min · mg_{cat}), p = 1 bar.

Acknowledgments
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Stability of Fe-based Fischer-Tropsch Catalysts at dynamic reaction conditions captured by in-situ magnetometry

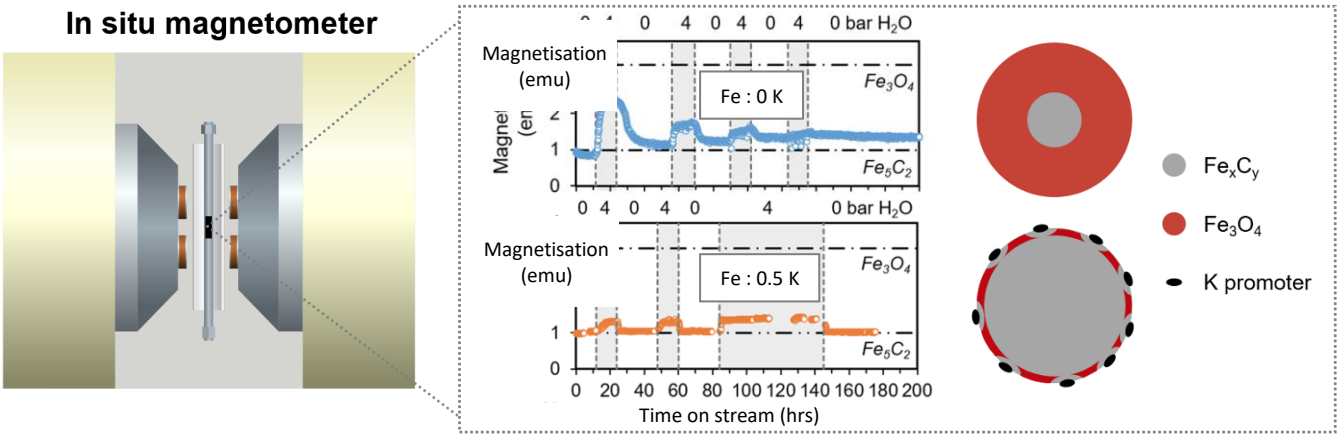
Q. Chang[1,2], R. Stegman[1], N. Fischer[1], H. Kotzé[1], D. de Oliveira[1], C. Zhang[2], J. Xu[2], X. Wen[2], Y, Yang[2], Y.W. Li[2], H. Niemantsverdriet[3], K.-J. Weststrate[3], Michael Claeys[1,*]

[1] *Catalysis Institute and c*change), University of Cape Town, Cape Town, South Africa*
[2] *Synfuels China Technology Co., Ltd., Huairou, Beijing 101407, the People's Republic of China*
[3] *SynCat@DIFFER, Syngaschem BV, P.O. Box 6336, 5600HH Eindhoven, The Netherlands*
[*] *Michael.Claeys@uct.ac.za*

Introduction. The Fischer-Tropsch process can play a crucial role in converting carbonaceous feedstock into sustainable fuels and chemicals. It is operated in large scale plants using cobalt and iron-based catalysts. Iron-based catalysts are particularly suitable for the Fischer-Tropsch synthesis using biomass-derived syngas due to its high water–gas shift activity, flexible operating conditions, and its low cost[1]. During its use the catalysts will be exposed to a range of reaction environments, which include dynamically changing conditions when feedstocks from renewable sources are employed. Although controversy regarding the active phase in iron-based catalysts still exists, it is generally accepted that iron carbides are the active phase; while magnetite is inactive[2]. Water, one of the main products formed in Fischer-Tropsch synthesis, is thought to have a significant influence on phase composition and catalyst stability[3]. Studies have shown that the presence of water results in the oxidation of the iron carbide phase to magnetite[3], which results in catalyst deactivation[2].

Experimental/methodology. In this work the oxidation threshold of relatively pure unpromoted and K-promoted Hägg carbide catalysts as well their response to dynamic changes of the reaction environment/water partial pressure has been determined using *in situ* magnetometry[4]. The reaction has been conducted at 275°C, the reaction temperature used for medium temperature Fischer-Tropsch synthesis. The oxidation of the carbide can be detected via an increase of magnetisation due to the formation magnetite and its reversibility via a corresponding decrease of magnetisation. Importantly, these observations can be done at fully relevant industrial reaction conditions.

Results and discussion. Oxidation thresholds could be determined as being in the range of 3-4 bar of water, and potassium promotion of the catalysts was found to suppress the onset of this oxidation. This process was largely reversible and limited to surface near regions in of the catalyst promoted with medium levels of potassium (see figure). The results obtained will be discussed in conjunction with catalyst performance data.



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Operando X-Ray Absorption Spectroscopic Investigations on Ni and Cu Catalysts for CO_2-Hydrogenation

Lorena Baumgarten[1,2], Jil Gieser[3], Patrik Hauberg[4], Malte Behrens[4], Erisa Saraçi [1,2], Jan-Dierk Grunwaldt[1,2,*]

[1]*Institute for Chemical Technology and Polymer Chemistry (ITCP), and* [2]*Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*

[3]*University Duisburg-Essen, Duisburg, and* [4]*Kiel University, Institute of Inorganic Chemistry Kiel, Germany*

[*]Corresponding author: *grunwaldt@kit.edu*

Introduction:

The key to achieve a substantial reduction of CO_2 emissions into the atmosphere to counteract the man-made climate change is the employment of renewable energy resources. A promising approach for renewable energy storage is "Power-to-Liquid" concept (cf. www.spp2080.org): green H_2 and CO_2 either from local sources or the atmosphere are transformed into chemicals and fuels, like methanol. Currently, methanol is mostly produced from a fossil syngas as feedstock (CO, CO_2 and H_2), using a $Cu/ZnO/Al_2O_3$ catalysts (CZA). Switching to pure CO_2 as carbon feedstock brings new challenges. CO_2-hydrogenation is thermodynamically less favored compared to CO hydrogenation and leads to higher water formation. Both CO_2 and water deactivate the classical CZA catalyst. Modification by Ni and Ga is very promising for novel methanol catalysts which may help overcome CZA limitations.[1,2] Operando X-ray absoprtion spectoscopy (XAS) is a powerful tool to unravel the structural dynamics of novel CO_2-hydrogenation catalysts.

Experimental:

Coprecipitated Cu/Ga_2O_3 (CG) and Ni/Ga_2O_3 (NG) with high metal loading > 50% were investigated *via operando* XAS experiments with the aim to study the catalyst structure during CO_2-hydrogenation to methanol. The experiments were carried out at 30 bar with a novel high pressure cell.[3]

Results and discussion:

Activity tests of CG and NG showed an increased methanol formation compared to the reference Zn-promoted Cu/MgO model catalyst.[4] Hereby, the CG catalyst shows 100% methanol selectivity and high production rates. To better understand the superior performance of this catalyst, *operando* XAS-studies were conducted, including a H_2-dropout experiment. During H_2-dropout a slight decrease in methanol formation due to deactivation was observed. A following H_2 treatment could not restore the initial activity of the reduced catalyst. The selectivity towards methanol, however, stayed at 100%. According to operando XANES, there are no changes in the oxidation state of the catalyst during reaction and H_2-dropout detectable. Moreover, XANES/EXAFS revealed that switching the reaction conditions did not cause changes in the electronic environment of the Cu species (Figure 1). Hence, the bulk structure of the Cu particles is stable towards oxidizing conditions. To further increase the surface sensitivity now catalysts with smaller copper particles, prepared by flame-spray pyrolysis, are used to investigate the catalyst response to dynamic changes of the gas composition. Promotional effects of Ga on Cu surface and Ni bulk affecting the methanol selectivity, e.g. the formation of intermetallic Ni-Ga,[1] will be discussed in our contribution.

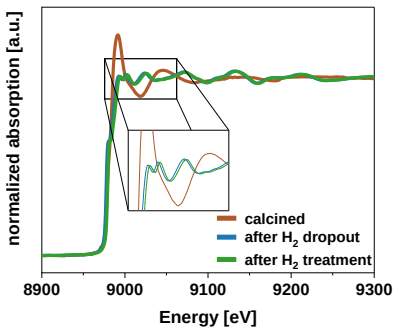

Figure 1: XANES/EXAFS spectra of CG before reduction, after reaction followed by H_2-dropout and after the second reduction.

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Separation and conversion of CO_2 to methanol over bifunctional catalysts under dynamic reaction conditions

Huidong Xu, Johannes A. Lercher and Andreas Jentys
School of Natural Sciences and Catalysis Research Center, Technical University of Munich, Germany

Keywords: CO_2 capture and hydrogenation, bifunctional catalysts, dynamic processes

Introduction CO_2 is the main component of greenhouse gases and its increasing concentration in the atmosphere is a critical environmental issue. Thus, novel integrated processes for the capture and conversion of CO_2 into chemicals and fuel components under dynamic reaction conditions are required to provide the necessary flexibility for fluctuating and non-stationary energy demands.
In this presentation, we present a combined sorbent and catalyst with dual functionality containing base and metal sites for CO_2 sorption and subsequent conversion to methanol.

Experimental/methodology The catalysts are based on ordered mesoporous polymers [1] acting as supports for amino groups (CO_2 adsorption sites) and for size-controlled Pt nanoparticles (CO_2 hydrogenation sites). The capacity for CO_2 sorption and the activity for the subsequent hydrogenation to methanol were measured using a fixed bed tubular reactor at 1 bar and temperatures between 70 and 120 °C, applying dynamic changes in the reactant feed to simulate the periodic operation of a CO_2 (pressure swing) absorber.

Results and discussion The reaction was carried out in a two step process. CO_2 was adsorbed at 70 °C until equilibrium was reached. After removing the physisorbed CO_2 by purging, the gas flow was switched to H_2 in He and the temperature was increased from 70 to 120°C during CO_2 hydrogenation. Although methanol formation was already observed at the CO_2 sorption temperature (70 °C), it was necessary to increase the temperature to 140 °C to completely remove all products from the catalyst (see Figure 1). A conversion of CO_2 to methanol of 25%, based on the irreversible CO_2 sorption capacity, was observed. Methanol and water were the only products formed, CO and CH_4 were not detected in any of the experiments.

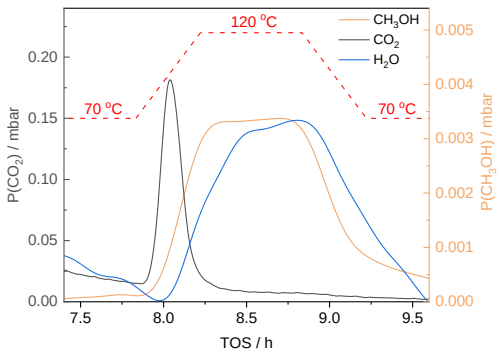

Figure 1: Product formation during temperature increase for Pt-loaded sorbent/catalyst

CO_2 sorption capacity and catalytic activity were influenced by the type of amine used (i. e., primary, secondary and bi-basic). The use of ordered mesoporous polymers increased the methanol yields compared to the SiO_2-based catalysts previously studied [2].

Acknowledgments *We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support through SPP2080 (project number JE-260/13-1).*

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Elucidation of the Dynamics of Thermally Stable Single Atom Catalysts

Yong Wang[1,2*], Dong Jiang[1], Xuelong Wang[3], Abhaya Datye[4], Ping Liu[3]
[1]*The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, USA*
[2]*Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, WA 99354, USA*
[3]*Chemistry Division, Brookhaven National Laboratory, Upton, New York 11973, USA*
[4]*Department of Chemical and Biological Engineering and Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, NM 87131, USA*
[*]*wang42@wsu.edu*

Introduction. Supported precious metals with atomic dispersion have proved promising for achieving maximum atom efficiency as well as improved activity and selectivity in catalyzing a growing number of thermo-, electro-, and photo- driven chemical reactions. We have recently reported the synthesis of thermally stable single atom catlaysts by atom trapping [1] and by confinement of single atoms using nanoglues [2]. Modificaiton of support surface by single atom trapping was found to form 2-D metal rafts, exhibiting enhanced reactivity [3]. We further found that these stablized single atoms can be readily activated by steam treatment [4] or thermal-shock treatment [5]. However, single atom catalysts are dynamic and undergo changes in their coordination, leading to altered reactivity patterns.

Experimental/methodology. Single atom catlaysts were synthesized using atom trapping [1]. A theory-guided approach along with spectroscopy and microscopy was used to identify the active sites in CO and methane oxidation.

Results and discussion. Dependence of turnover frequencies (TOFs) on CO partial pressure (pCO) from 0.5 to 4 kPa was studied on single atom 1 wt % Pt_1/CeO_2 catalyst prepared by atom trapping (Figure 1a). At 300 °C, CO partial pressure (pCO) was varied between 0.5 to 4 kPa while O_2 partial pressure (pO_2) was kept at 10 kPa. As shown in Figure 1b, under exactly the same pCO (1 kPa) and pO_2 (10 kPa), two stable working states (point-B vs. point-D) were observed with one order of magnitude difference in TOFs. With integrated kinetic studies, operando spectroscopies, and density functional theory calculations, we clarified the dynamic behaviors and reaction pathways under the lean CO oxidation condition. We found that different thermodynamically stable phases exist at critical CO and O_2 pressures, leading to varied adsorption configurations over isolated Pt_1 on CeO_2. Such dynamically responded boundaries dictate the reaction pathways involved and reactivity of single atom catalysts. We further discovered that a Langmuir-Hinshelwood mechanism via a carbonate-like intermediate prevails over single atoms on a reducible support, leading to a reduced reaction barrier by half compared to the typical Mars-van Krevelen mechanism and, thus, an increased turnover frequency by one order of magnitude.

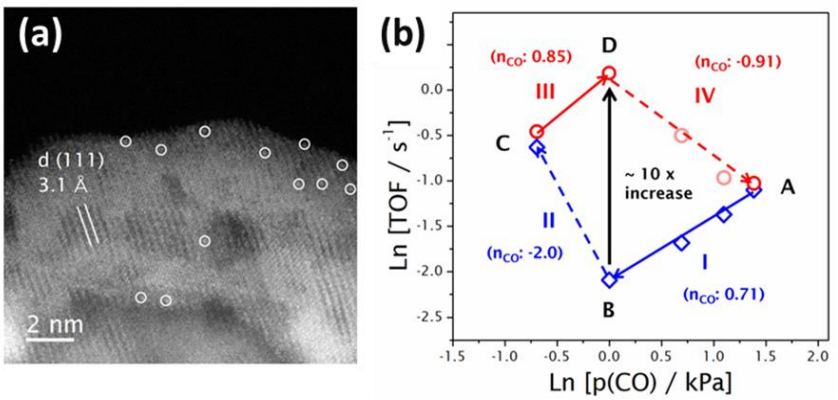

Figure 1 (a) AC-STEM images of 1 wt % Pt_1/CeO_2 catalyst prepared by atom trapping showing the presence of atomically dispersed Pt on CeO_2 (111) step edges. (b) Dependence of CO oxidation rate on the partial pressure of CO on 1 wt % Pt_1/CeO_2. Conditions: 10 % O_2. 0.5-4 % CO. 300 °C.

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Simultaneous CH_4 and N_2 Conversion under Microwave and Microwave Plasma Catalytic Processing

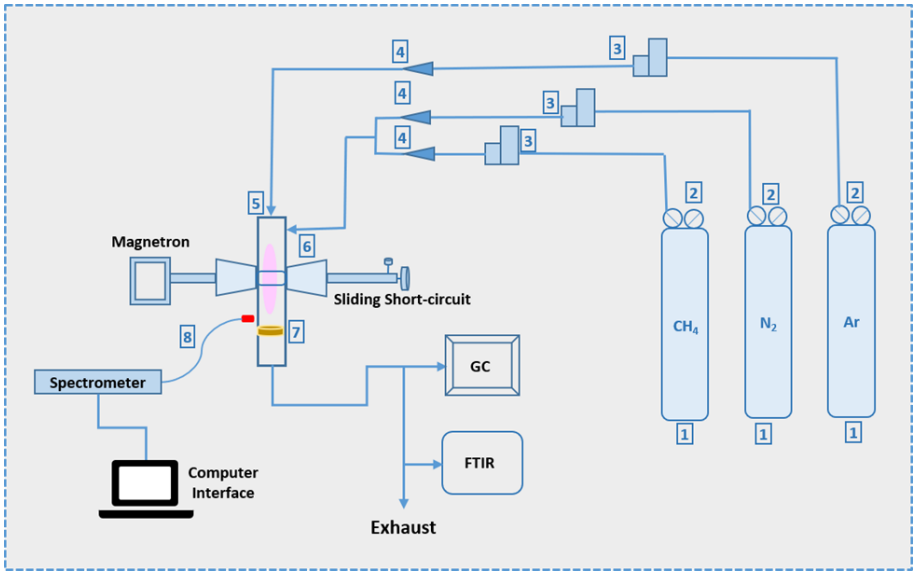
Sarojini Tiwari, Jianli Hu*
Department of Chemcial & Biomedical Engineering, West Virginia University
**john.hu@mail.wvu.edu*

Introduction

Chemical processing industry is substantially dependent on natural gas as a feedstock. In the process, it has become one of the major contributors of green-house gas emission. Process intensification can substantially upgrade chemical industries to a carbon free and zero waste systems. The basic definition of an intensified chemical process has broadened from merely reducing the size of the processing plant to a holistic undertaking that can reduce waste and energy consumption with improved product yield. The direct conversion of Methane (CH_4), the major component in shale gas, to value-added chemicals can be qualified as an intensified process, if it is energy efficient, free of unwanted side products (CO_2), and leads to maximum conversion of CH_4 to useful products.

Experimental/methodology

Microwave catalytic reaction can activate CH_4 and N_2 simultaneously to produce NH_3 and C_2 products in a single step process, represented schematically in Figure below. The reactor system can be operated in two scenarios: microwave only and microwave plasma. The reactor system is equipped with optical emission spectrometer (OES) to measure surface plasma species and online MS and FTIR to quantify the products.



Results and discussion

Two highly stable molecules, CH_4 and N_2 were simultaneously activated in a single-stage microwave-heated catalytic reactor to form ammonia, ethane, ethylene, and acetylene at atmospheric pressure. Density functional calculations and micro-kinetics modelling were used to predict the reaction behavior at temperatures ranging from 573 K to 973 K and validated with experimental analysis. The influences of terrace (111) and step (211) sites on K promoted Ru crystals were established in product formation and catalyst coking. NH_3 formation occurs predominantly on the step (211) sites while C_2 product formation can occur on both the sites. It was found that the elementary reaction steps leading to NH_3 synthesis occurs due to the non-thermal effects of microwave irradiation while C_2 products formed simultaneously are due to the thermal effects only. A reaction mechanism is postulated on the catalyst coking and validated experimentally by in-situ regeneration using H_2 and O_2.

The main challenge in simultaneous conversion of methane and nitrogen to ethylene and ammonia under plasma conditions is the low selectivity. This is largely due to the difficulties in controlling the reactions among the intermediates. To address this challenge, this article explored an innovative strategy - post-plasma catalysis in a microwave-enhanced plasma (MWP). After placing the thermally heated CeO_2 catalyst in the post plasma region, the active nitrogen-based species generated a steady amount of ammonia (selectivity=9%). The selectivity of ethylene increased from 3% to 37%, the highest among the C_2 products. While under conventional thermal heating, in the absence of plasma, the catalyst over-hydrogenated the acetylene to ethane and no ammonia was produced from nitrogen.

Elucidating the role of metallic Fe and Fe_3O_4 on the in-situ formation of steady-state phases responsible for efficient CO_2 hydrogenation to higher hydrocarbons

L. Kraußer, H. Lund and E. V. Kondratenko*

Leibniz-Institut für Katalyse e.V., Albert-Einstein-Str. 29a, 18059 Rostock, Germany
**Evgenii.Kondratenko@catalysis.de*

Keywords: CO_2 Hydrogenation, Fischer-Tropsch Synthesis, Iron Nanoparticles, Heterogeneous Catalysis

Introduction. The CO_2 Fischer Tropsch Synthesis (CO_2 FTS) requires a catalyst that is active for both the conversion of CO_2 to CO and subsequent CO hydrogenation to hydrocarbons with minimal CH_4 selectivity. In this regard, bulk or supported Fe-based catalysts are widely used but require activation through reductive pretreatment resulting in various Fe-containing phases, which are distributed inhomogeneously along the catalyst bed.[1] This way, it is challenging to control the steady-state catalyst phase composition which, however, affects the catalytic activity and product selectivity. Therefore, we present a facile and swift catalyst preparation method consisting of physical mixing Fe nanoparticles, Fe_3O_4 and promoters without any form of pretreatment to analyze reaction-induced phase changes and the resulting consequences on catalytic performance. This knowledge is necessary to enable purposeful preparation of catalysts with hindered CH_4 formation.

Experimental. Fe_3O_4, alkali metal promoters, e.g., K_2CO_3, Na_2CO_3, and metallic Fe (particle sizes: 30-40 nm (Fe^a), 90-100 nm (Fe^b) and 790 nm (Fe^c)) were obtained commercially. The materials were mixed physically using a mortar (molar ratio Fe/Fe_3O_4 = 0, 1, 2, 4, 8; K/Fe = 0.01) and tested directly for CO_2 hydrogenation at 300 °C and 15 bar without any pretreatment using a feed with a H_2/CO_2 ratio of 3.

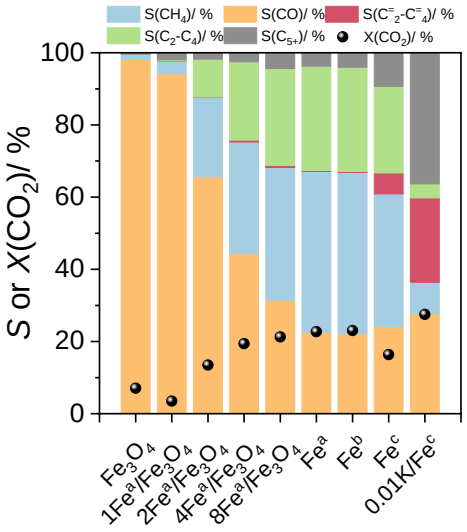


Fig. 1: Catalytic properties for CO_2 hydrogenation. Conditions: 300°C, 15bar, $3H_2/CO_2/0.3N_2$, 6 mL/min; particle size Fe^a=30-40nm, Fe^b=90-100nm, Fe^c=790nm

Results and discussion. The catalysts consisting of pure α-Fe nanoparticles are not only more selective towards higher hydrocarbons (C_{2+}) than the Fe_3O_4-containing samples but also exhibit a significantly higher CO_2 conversion (Fig.1). In fact, both CO_2 conversion and C_{2+} selectivity decrease drastically with increasing Fe_3O_4 content in the Fe/Fe_3O_4 mixtures. This indicates that Fe_3O_4 is not required in the initial catalyst composition to enable CO formation, which challenges conclusions from previous literature stating that Fe_3O_4 is the active phase catalyzing the conversion of CO_2 to CO under the applied conditions.[2] We put forward that Fe carbides (Fe_xC_y) formed in situ from α-Fe catalyze this reaction instead. By physically mixing K_2CO_3 with α-Fe nanoparticles (0.01K/Fe^c), CH_4 formation can be suppressed significantly (9% selectivity at 28% CO_2 conversion) likely due to electronic promoter effects on the hydrogenation ability of Fe_xC_y.[1] The selectivity to higher hydrocarbons (C_{2+}) and lower olefins ($C_2^=$-$C_4^=$) increases to 64 % and 23 %, respectively. These results are comparable to those reported on state-of-the-art Fe-based catalysts which, however, require time- and cost-intensive pretreatment.[3] Operando XRD studies are in progress to elucidate the mechanism and kinetics of reaction-induced α-Fe conversion into steady-state phases including their spatial distribution. Steady-state isotopic transient kinetic analysis will provide the lifetime and concentration of active species yielding CO and CH_4.

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Dynamic hydrogen release from LOHC using a highly efficient catalyst coating

*Phillip Nathrath[1], Benjamin Baier[1], Yousuf Raed Ramzi[1], Jannis Müller-Ebhardt[2], Peter Wasserscheid[1], Eike Hübner[3], Patrick Schühle[1]**

[1] *Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen/Germany*
[2] *Kelvion PHE GmbH, Sarstedt/Germany*
[3] *Fraunhofer Heinrich-Hertz Institute, Goslar/Germany*
**patrick.schuehle@fau.de*

Introduction: In this work, the concept of a catalytic plate reactor (CPR) is followed as a combination of a plate heat exchanger and a chemical reactor. The CPR consists of metal plates that are coated with a catalytically active layer on one side and heated from the backside. The liquid feed is continuously flowing through the slit between the plates. The high thermal conductivity of the metal plates and the direct contact to the catalytic surface avoid temperature gradients, enabling fast heat-up and cool-down cycles.[2] Therefore, a CPR is suitable for quick start-stop cycles, as required, e.g. for dynamic operation scenarios. Furthermore, CPRs have a low pressure drop, faciliating a fast gas transport. A major challenge in the realization of CPRs is the production of mechanically stable and active coatings. We have devised a method that is based on spray-coating a sol-gel composite ceramic dispersion to address this issue. Our catalytically activated plates are tested for the endothermic dehydrogenation of the hydrogen storage molecule perhydro-benzyltoluene (H12-BT) as an example reaction to emphasise the benefits of the CPR-concept. This study covers large parts of the development chain of a CPR, starting with the evolution and analysis of catalyst coatings, testing their dynamic performance in a small-scale continuous set-up, and finally scaling up to a CPR of technical size.

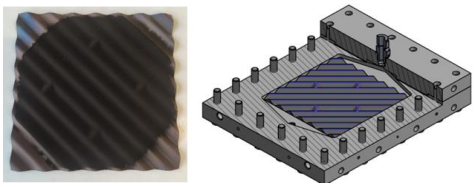

Figure 1: Embossed metal plate after coating (a); CAD-Drawing of the used CPR

Experimental: For the catalytic activated plates, a planar metal plate is spray-coated with a self-developed sol-gel-composite dispersion, which forms a porous metal oxide support layer, when calcined. By a Design of Experiments (DoE) approach the mechanical stability and coating load were greatly enhanced. Simultaneous a good sprayability of the dispersion was maintained. With the novel recipe, the prepared plates can reach a coating thickness of up to 500 µm without crack formation. After a successful coating and calcination, the catalyst precursor platinum sulphite acid is impregnated onto the support layer and subsequently reduced under hydrogen.

Results and discussion: In addition to planar substrates, three-dimensional embossed plates that improve hydrodynamics (see Figure 1), can be coated, using our highly flexible spray coating process. These plates were tested in a new designed CPR at temperatures between 280 °C and 320 °C and elevated pressures of up to 3 bar. The results of the reaction condition optimization for this CPR-module are shown in Figure 2. At a temperature of 310 °C and a pressure of 1.5 bar, a high conversion of >50 %, suitable for technical application is reached. The catalyst showed no significant activity loss during 20 h of operation, making a further scale-up of this catalytic reactor concept highly attractive.

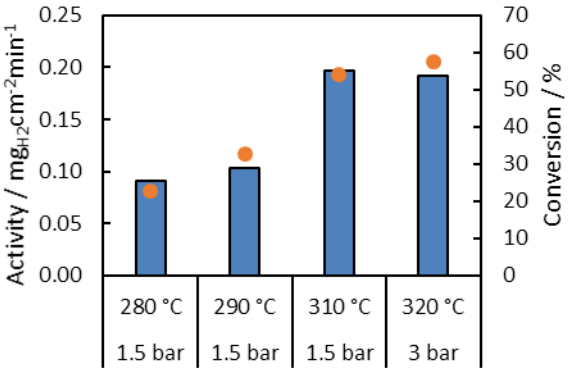

Figure 2. Continuous dehydrogenation experiments in a CPR (feed = 1 $g_{H12\text{-}BT}$ min^{-1}; m_{cat} = 6.93 g; catalyst = 3.63 wt.% Pt-S/Al_2O_3).

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Sulfur tolerance of Na-Ru/Al_2O_3 dual function material during the cyclic CO_2 capture and catalytic methanation

S. Cimino[1*], E.M. Cepollaro[1], L. Lisi[1]

[1]*STEMS- CNR, Napoli, Italy*
[*]*stefano.cimino@cnr.it*

Keywords: CO_2 capture and utilization, Power to gas, Chemical looping, Sulfur poisoning

Introduction

Converting CO_2 captured from flue/process gases or even from air using green hydrogen made from renewable energy is a way to contribute to reaching the ambitious decarbonization goals set for 2050 and also a valuable solution to store excess electrical energy in fuels/chemicals solving the intrinsic variability of renewable sources [1]. The integrated CO_2 capture and methanation with Dual Function Materials (DFM) is emerging as a vibrant field of research for its potential to increase the efficiency and reduce the cost of current multistage CCU processes [2]. However, testing the S-tolerance and durability of DFMs during prolonged cyclic operation with feeds containing sulfur impurities is an area requiring detailed investigation before the integrated process is to be scaled up to applications [1]. In this work, we set out to investigate for the first time the effect of sulfur poisoning during the cyclic CO_2 capture and methanation performed over a Sodium-Ruthenium on γ-Al_2O_3 DFM, which is reported among the best performing formulations at mid-low temperatures [1-3].

Experimental/methodology

Ru and Na were dispersed sequentially inside 1mm Al_2O_3 spheres by impregnation with nitrate precursors. Their loadings in the final DFM were deliberately kept low (ca. 1 % and 2.8 % wt., respectively) to better highlight the possible sulfur-poisoning effects on both the sorption and catalytic functionalities during prolonged operation in a fixed bed reactor at 300 °C with alternate feed conditions [3]. In particular, we present the results obtained during several repeated cycles carried out with the simultaneous presence of CO_2, H_2O, O_2, and SO_2 (10–100 ppmv) in the process gas stream to assess the impact of sulfur poisoning on CO_2 adsorption and conversion, methane productivity and selectivity, as well as the fate of sulfur under relevant operating conditions. The main physicochemical properties of the fresh and sulfated DFM were correlated with the results from catalytic hydrogenation tests of either preadsorbed or gas phase CO_2 and in-situ DRIFT study. Eventually, we preliminarily investigated possible regeneration strategies for a heavily sulfated DFM.

Results and discussion

Cyclic operation with SO_2 (10–100 ppmv) and O_2 in the flue gas demonstrated a remarkable sulfur tolerance of the DFM in the integrated process under both dry and humid feed conditions. In particular, during the CO_2 capture step, the DFM completely removed SO_2 storing it as sodium sulfates, which are rather stable species at 300 °C and were only marginally converted to H_2S during the subsequent catalytic methanation step, thus avoiding severe poisoning effects. However, the accumulation of S above ca 100 µmol/gDFM progressively reduced the CO_2 adsorption capacity of the DFM that tended to vanish when its strong basic Na-sites were finally saturated by sulfates. Careful analysis of transient methanation tests of gas phase and/or pre-adsorbed CO_2 coupled to the in-situ DRIFT results on the fresh and sulfated DFMs suggested the occurrence of a peculiar and favorable self-regeneration mechanism for the catalytic Ru sites, preserving them from any significant sulfur poisoning effect.

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Enhanced $Ca_2Fe_2O_5$ Composites for Chemical Looping Reforming of Methane

A. Strazzolini[1], M. Boaro[1*], C. de Leitenburg[1], A. Trovarelli[1]

[1]Dipartimento Politecnico, Università degli Studi di Udine, 33100 Udine, Italy.
[*]*marta.boaro@uniud.it*

Keywords: H_2 generation, chemical looping, oxygen carrier, steam methane reforming, calcium ferrite oxides, ceria-zirconia.

Introduction. Chemical Looping Reforming (CLR) of methane using an oxygen carrier (OC) mediator has recently gained the interest of the scientific community, since this multi-step process could afford higher efficiency of current syngas production technologies and overcomes some of their issues, such as CO_2 emissions from burners, high steam consumption and high energy demand for air separation [1]. $Ca_2Fe_2O_5$ has proven to be a valid alternative to single Fe-oxides as oxygen carrier, due to higher phase reversibility as well as a lower equilibrium pO_2 [2]. The aim of this work is to boost the activity and stability of $Ca_2Fe_2O_5$ in methane steam reforming-chemical looping cycles (MSR-CL) through the implementation of a catalyst-assisted process [3] based on Ni-promoted $Ca_2Fe_2O_5$-$Ce_{0.8}Zr_{0.2}O_2$ composites.

Experimental/methodology. $Ca_2Fe_2O_5$ (C2F) and $Ce_{0.8}Zr_{0.2}O_2$ (CZ) were prepared by coprecipitation route. Catalyst-assisted OCs were prepared by incipient wetness impregnation of $Ni(NO_3)_2$ aqueous solutions selectively into CZ (iCZ) or C2F (iC2F). A Ni doped C2F (dC2F) was also prepared via Pechini synthesis. The composites (iC2F-CZ, C2F-iCZ and dC2F-CZ) were prepared physically mixing the single carriers and keeping Ni/Fe molar ratio constant to 0.025. Materials were characterized by means of XRD, BET, TGA, SEM-EDS. Chemical looping tests (800 °C, GHSV≈20'000 h^{-1}, 0.2 g of sample) were performed in a microreactor facility equipped with a mass spectrometer. Fig 1. shows the feed conditions of a typical CL test cycle.

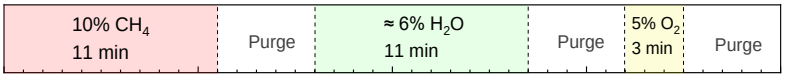

Fig 1. CL test cycle feed conditions (reactant concentrations and steps times).

Results and discussion. Preliminary results on composites materials without the addition of Ni agreed with literature reports [4]. CZ addition to C2F has beneficial impact on both steps of MSR-CL with the best performance obtained for the composite having a C2F:CZ mass ratio equal to 1. All catalyst-assisted samples reacted faster with CH_4 in comparison to unpromoted samples. The best results were achieved with the C2F- Ni impregnated CZ composite (C2F/iCZ), which shows a nearly tripled CH_4 conversion and hydrogen production by water splitting (Fig. 2), the highest CO selectivity and the lowest carbon deposition during reduction. The interplay between the two constituents of this composite was investigated by comparing different OC bed configurations, i.e. single bed composed by mixed C2F and iCZ vs. layered dual bed, made interposing a glass wool plug between the unmixed components. The mixed composite exhibited similar initial fuel conversion and the lowest tendency toward carbon formation, but its performances decreased significantly over cycles in comparison to what was found for the DB configurations. Based on spent samples observations (XRD, H_2-TGA), a different structural evolution of the C2F in the mixed bed configuration is hypothesized. Further characterization and tests are underway to unravel the mechanism behind the steady deactivation of the composite and to understand the key parameters that could, on the contrary, contribute to its optimization.

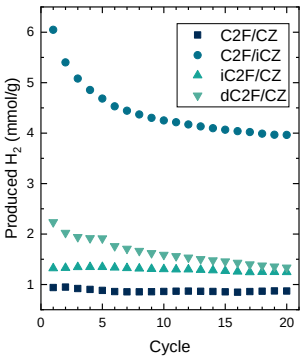

Fig. 2. Specific hydrogen production of catalyst-assisted composite OCs during steam oxidation step. Prior to the test, samples were subjected to five reduction/oxidation cycles at 850 °C, exposing them alternatively to 5% H_2 and 5% O_2.

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Stabilization of epitaxial OER catalysts by engineering transition metal composition and stacked layer geometries in perovskite oxides

A. Kaus[1*], M. Maksumov[2], Z. Teng[3], L. Heymann[1], K. Kleiner[3], F. Hausen[2], F. Gunkel[1]

[1] *Peter Gruenberg Institute 7 (PGI-7) and JARA-FIT, Forschungszentrum Juelich GmbH, Juelich, Germany*
[2]*Institute of Energy and Climate Research-Fundamental Electrochemistry (IEK-9) and JARA-Energy, Forschungszentrum Juelich GmbH, Juelich, Germany*
[3]*Muenster Electrochemical Energy Technology (MEET), University of Muenster (WWU), Muenster, Germany*

[*]*a.kaus@fz-juelich.de*

Keywords: water electrolysis, oxygen evolution reaction, perovskite oxides, electrocatalyst, epitaxial model catalysts

Introduction. The bottleneck of electrochemical water splitting is the oxygen evolution reaction (OER). The high overpotential and limited stability at this half-reaction hinder the economical energy conversion. Active materials with a lower overpotential are less stable and stable materials require higher overpotentials to trigger the OER.[1] Epitaxy allows the combination of a stable but less active material with an active material with limited stability as well as a precise variation of the chemical composition of the catalyst and thus the active transition-metal oxygen bonds/hybrid electronic states.[2]

Experimental/methodology. The model catalysts were fabricated by pulsed laser deposition (PLD) to achieve well-defined model catalysts with defined thin film thicknesses. The surface morphology maintained similar while the chemical and structural composition of the catalysts were varied. The crystallinity and strain were investigated by x-ray diffraction (XRD) and reciprocal space mapping (RSM) before and after the OER. The measurement of the activity and stability of the superlattices were performed with cyclic voltammetry (CV) and chronopotentiometry (CP) in alkaline environment (0.1 M KOH) with a standard-three electrode setup.

Results and discussion. Based on the epitaxy approach we can correlate chemical composition, layer thickness, and electronic structure to OER activity and stability parameters. We find that the transient behavior of perovskite-type OER catalysts can be tuned by the chemical composition and detailed geometry of the epitaxial catalyst. As we find, a superlattice structure in which we layer a particularly stable material and an active oxide, leads to enhanced stability of the catalyst, while maintaining significant OER activity of the superlattice.

Acknowledgments
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Hydrogen charge/discharge cycles via formic acid on Pd/activated carbon catalyst

Maria Ribota Pelaez, Maria Isabel Dominguez Leal, Miguel Angel Centeno, S. Ivanova*

Instituto de Ciencias de Materiales de Sevilla, Centro mixto CSIC- Universida de Sevilla, Avda. Americo Vespucio 49, 41092 Sevilla, Spain

sivanova@us.es

Keywords: hydrogen, formic acid, charge/discharge cycle

Introduction. The problems associated to the "greenhouse effect" have raised the social awareness towards CO_2 emissions minimization and orientation of the energy models to carbon dioxide free energy sources. Thus, nowadays the hydrogen is atracting all attention as green fuel, being the only warning associated to its transportation and storage. In this regard the use of liquid organic hydrogen carriers (LOHCs), such as formic acid (FA), presents a possible solution to this warning. Although containing only one hydrogen molecule per molecule and lower hydrogen density compared to the others LOHCs, the FA shows several important advantages; i.e. it can be synthesized directly from the lignocellulosic biomass or by hydrogenation of CO_2, being the later considered as an effective technology to deal with the CO_2 emissions control. The success of such a technology relies on the use of green hydrogen produced using renewable energy and one unique catalyst that could assure the charge (CO_2 hydrogenation to formic acid) and discharge (formic acid dehydrogenation) hydrogen cycles. That is why, this study dedicates to the preparation, characterization and activity of paladium based catalysts for the reaction of CO_2 hydrogenation to formic acid and its dehydrogenation to hydrogen gas.

Results and discussion. A series of Pd catalysts have been prepared and tested separately in both reactions. The variations of active phase nature and loading, support nature and reaction parameteres have been carried out in order to obtain an optimal performance in both reactions. Once the catalysts selected, the charge/discharge cycles are performed. One example is presented in Figure 1, using a 10%Pd/activated carbon (AC) catalyst.

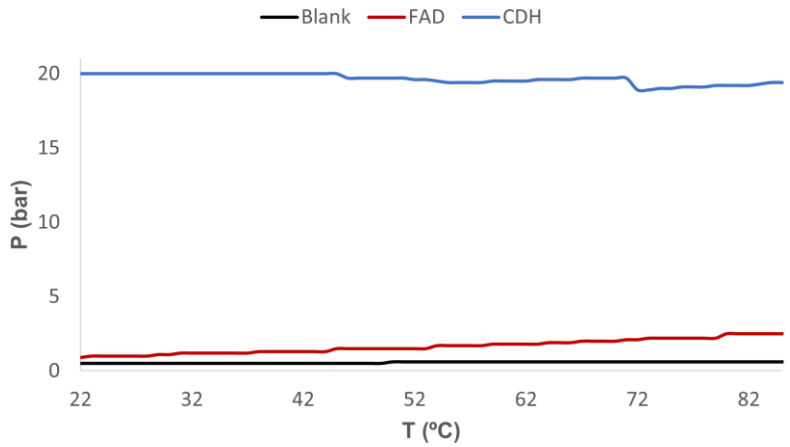

Figure 1. Charge/discharge cycle over 10%Pd/AC catalyst.

The first stage of the cycle, the dehydration of formic acid, is carried out at different temperatures and the formation of gas (CO_2 and H_2) increased continuously as a function of the reaction temperature. Once the cycle finished, the pressure is released and the CO_2+H_2 mixture is introduced in the reactor for the second cycle (CO_2 hydrogentation to FA) over the catalyst. The formic acid concentration, pH of the reaction suspension and pressure changes are monitored during the cycles and showed that the catalyst participates in both, charge and discharge reactions of hydrogen.

Acknowledgments

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Particle Size Effects in Ru/CNF Catalysts during Supercritical Water Gasification of Glycerol

David Baudouin[1*], C. Hunston[1,2], L. Koning[1], A. Agarwal[1,3], O. Kröcher[1,2], F. Vogel[1,4]

[1] Bioenergy and Catalysis Laboratory, PSI, Villigen, Switzerland;
[2] Institute of Chemical Sciences and Engineering, EPFL, Lausanne, Switzerland;
[3] School of Architecture, Civil and Environmental Engineering, EPFL, Lausanne, Switzerland;
[4] Institute for Biomass and Resource Efficiency, FHNW, Windisch, Switzerland.
** david.baudouin@psi.ch*

Keywords: Ruthenium nanoparticles, Methanation, Particle size effect, Supercritical water gasification, Catalyst stability

Introduction. Supercritical water gasification (SCWG) of wet biomass has drawn considerable attention in recent years as a clean and renewable synthetic natural gas production technology.[1] Ru has proved to be the most performant active phase for such reaction.[2] At nanoparticle surface, "hollow" ruthenium sites allowing high coordination of CO (*B5* sites) proved lower CO dissociation energy barriers.[3] A DFT study showed that 1.5 nm Ru NPs supported on graphite contained more of these sites than 1.0 nm Ru NPs.[4] These findings are in line with the high SCWG activity observed with Ru/C catalysts composed of small Ru NPs (1.2-1.4 nm)[5], indicating a structure sensitivity for this reaction. However, the geometry of a particle is known to greatly depend on the atmosphere it is exposed to, even at low partial pressures.[6] The effect of particle size on Ru activity in SCWG may therefore greatly differ from theory. Here, we will report the particle size effect in a model SCWG system, using Ru/CNF catalysts of different Ru NP sizes to gasify aqueous glycerol solutions to CH_4.

Experimental/methodology. A continuous fixed bed reactor was operated at 405–410 °C and 28.5 MPa using aqueous glycerol (6–20 wt%) at varying flows to control space flow velocity and maintain low conversion rates (kinetic regime).

Results and discussion. Ru/CNF catalysts of different Ru nanoparticle (NP) sizes (0.9-2.7 nm) were assessed for their performance in continuous supercritical water gasification (SCWG) of glycerol. A structure sensitivity of Ru was demonstrated, with high initial turnover frequencies (TOF) for Ru NPs smaller than 1.2 nm. Deactivation happens essentially through: 1) coking, which occurs more readily at low Ru surface densities and is limited to nanometric layers, and 2) sintering, which led to final NP sizes ranging from 2 to 3 nm independent of the catalyst loading (1 to 30 wt% Ru). A correlation between TOF and the density of surface Ru atoms was found, with an optimal surface density (0.4-0.7 $atom_{Ru,sfc}.nm^{-2}$) resulting in high initial and good steady-state TOFs, allowing longer lifetimes through the delay of coke formation. CNF as support enables high metal loadings, which could help in decreasing the costs of SCWG plants and hence make this technology even more attractive.

Acknowledgments
This project was financially supported by the Swiss National Science Foundation grants 200021_172624/1 and 200021_184817.

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Perovskite Oxides as Catalysts for Methanol Steam Reforming

T. Berger[1], J. Bock[2], F. Schrenk[1], H. Drexler[1], L. Lindenthal[1], C. Rameshan[1]

[1]*Chair of Physical Chemistry, Montanuniversität Leoben, Austria*
[2]*Institute of Materials Chemistry, Technical University of Vienna, Austria*

Keywords: catalysis, renewable energy, hydrogen storage,

Introduction. Methanol Steam Reforming (MSR) provides a promising solution for the storage and on-demand production of hydrogen for the utilization as an energy carrier in e.g.: Proton Exchange Membrane Fuel Cells (PEMFC). Due to the high reaction temperatures required and possible side reactions leading to the formation of carbon monoxide the use of suitable catalysts is of crucial importance. Even a proportion of 10 ppm carbon monoxide in the inlet gas can lead to a PEMFC performance loss of up to 80% [1]. A promising material for the reduction of the reaction temperature as well as high selectivity towards MSR are perovskite type oxides. These materials, with a general formula of ABO_3, display high resistance against agglomeration of nanoparticles socketed in the surface [2]. The composition of the catalyst can be specifically modified with suitable doping materials for the A- or B-site and can thus produce exsolved nanoparticles on its surface which fit the requirements necessary for MSR. [3]

Experimental. Different B-site doped (Cu, Ni, Co) perovskite type oxide catalysts in addition to the undoped basic structures of $Nd_{0.6}Ca_{0.4}FeO_3$ and $Pr_{0.6}Ca_{0.4}FeO_3$, were studied concerning their suitability for catalysing MSR. The onset temperature of the reaction of MSR as well as the selectivity of the individual catalysts against the production of carbon monoxide were of particular interest. As a result of the water saturated gas atmosphere a quantification of the reaction gases proved to be challenging. Therefore, a calibration strategy for a Mass Spectrometer (MS) was applied in combination with the development of a Python toolkit. This enabled us to quantify possible changes within the reaction atmosphere and compare the different investigated catalysts according to their catalytic activity. Additionally, operando XRD measurements at beamline P02.1. at DESY were conducted to investigate possible phase changes and deposition phenomena of carbon during the reaction.

Results and discussion. The experiments showed that each investigated material exhibited catalytic activity towards MSR regarding the yields of H_2 and CO_2 as well as a decrease in the reaction temperature. An increase in the catalytic activity could be tied to doping the B-site with the elements Ni, Co and Cu. Interestingly, the formation of CO at elevated temperatures could be observed in all catalysts examined, the degree depending on the basic structure and the doping material used. However, with catalysts doped with Cu high selectivity at lower temperatures for up to 370 °C could be observed towards the formation of H_2 and CO_2 instead of the unwanted side product CO, making them particularly interesting for further research in the on-demand production of hydrogen.

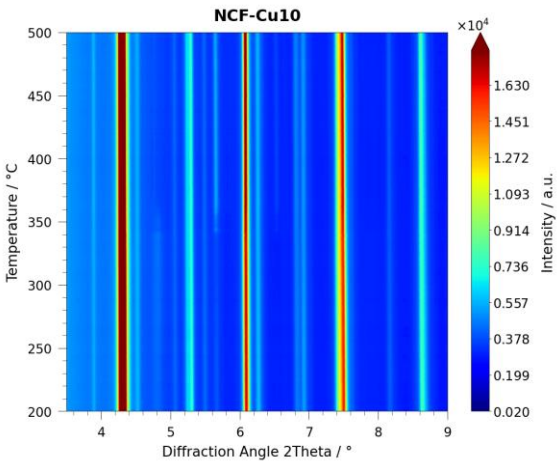

Fig. 1: Illustration of the operando XRD measurement during reaction conditions conducted at Beamline P02.1 at DESY (Hamburg) for $Nd_{0.6}Ca_{0.4}Fe_{0.9}Cu_{0.1}O_3$.

Acknowledgments
This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement n° 755744 / ERC - Starting Grant TUCAS)

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DFT investigation of the dynamics of Cu/ZnO, Cu/GaxOy, Ni/ZnO and Ni/GaxOy Catalyst under operating conditions

Claude Coppex, Jelena Jelić, Felix Studt

Karlsruher Institutit für Technologie, Karlsruhe, Deutschland
felix.studt@kit.edu

Keywords: DFT, CO_2toMet, Methanol , Cu/ZnO, surface dynamics

Introduction.

To reduce our carbon footprint Germany has vowed to reduce the CO_2 emissions by 40% until 2020 and 80% by 2050. To achieve this the electricity production of renewable energy needs to be increased drastically, which brings challenges to the electricity grid due to their fluctuating production time and the chemical industry which relies heavily on fossil derived substrates. Power2X summarizes projects concerned with the storage of electric energy in chemical energy usually involving carbon species. A very promising way for long-term and mobile storage is the conversion to a valuable chemical like Methanol, which has excellent storage properties and also serves as a base chemical. A renewable route for the production of methanol is the hydrogenation of CO_2/CO over the Cu/ZnO/Al_2O_3 catalyst. The mechanism has been under debate since the investigation of the catalyst for the process ~100 years ago.[1]

Experimental/methodology.

With theoretical modelling we investigate the surface dynamics of the "inverse" metal oxide/transition metal catalysts (Cu/ZnO, Cu/GaxOy, Ni/ZnO and Ni/GaxOy) under CO_2 hydrogenation conditions. For each of the metal oxide/transition metal systems we constructed a Phase diagram (Fig. 4) based on calculated alloy structures and the chemical potential of the gas phase. The thermodynamic stability of each system for the given reduction potential of a reaction mixture is a function not only of the heat of formation of the alloy/intermetallic compound but also of the reducibility of the metal oxide.

Results and discussion.

As a starting point, we studied the formation of surface (Fig. 2) and bulk alloys/intermetallic compounds. In all cases, the formation of a surface alloy is more favorable than a bulk alloy (Fig. 3). We will present a summary of the phase diagrams of not only the stable surface facet (111) and (100) but also other surface facets with lower coordination like (110) and (211). Once the degree of alloying of the surface is reduced to a few structures (those corresponding to the operating conditions from the Phase diagram) we will investigate the influence of alloying on relevant intermediates in the CO_2 hydrogenation process.

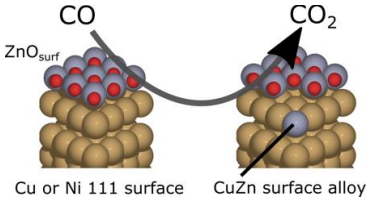

Fig 1. Schematics of how the reducing atmosphere under reaction conditions will form the surface alloy.

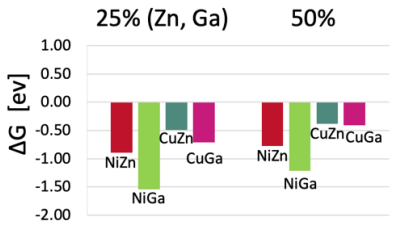

Fig 2. The Formation energy of the surface alloy compared to the bulk alloy.

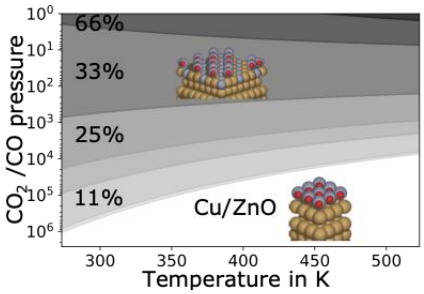

Fig 3. The calculated Phase diagram of the Cu/ZnO system.

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Chemical-looping application of Ni-Co/$MgAl_2O_4$ for syngas production by separate CH_4 decomposition and CO_2 activation

Yuchen Deng[1], Jong Wook Bae[1*]

[1]School of Chemical Engineering, Sungkyunkwan University (SKKU), Suwon, 16419, Republic of Korea

[*]E-mail: finejw@skku.edu

Keywords: Chemical looping; Ni-Co; mesoporous $MgAl_2O_4$; Methane decomposition; CO_2 activation.

Introduction. Global warming caused by emissions of greenhouse gases has become more deteriorating these decades, which leads to a growing importance of CO_2 conversion and utilization [1]. In 2015, Linde group revealed the pioneer pilot plants for a process named dry reforming of methane (DRM) which is able could transform two kinds of main greenhouse gases including CH_4 and CO_2 to syngas. Ni-based and Co-based catalysts are used in Linde Pilot Reformer (LPR). To promote the performance and longevity of these materials, the design of catalyst component and bulk structure is important, as well as investigation of the interactions between components [2]. Here, we proposed a new route to carry out the dry reforming of methane process by dividing the process into two parts including methane decomposition and reverse Boudourd of carbon dioxide. As methane decomposition into carbon and hydrogen occurred firstly followed by the coming of CO_2 feed gas which will react with the cardon on the surface of catalyst to carry out the reverse CO_2 boudourd reaction. In this way, deactivation caused by coke could be solved to some extent.

Experimental/methodology. The mesoporous $MgAl_2O_4$ and Ni-Co-Mg-Al_2O_3 materials were synthesized by evaporation induced self-assembly (EISA) method. The nickel and cobalt precursor were impregnated on the prepared supporter using the traditional dry impregnation method. All of the catalysts were calcined at 450 ^oC for 30 minutes with continue calcination at 800 ^oC for 2 h. A catalytic test on Ni-Co/$MgAl_2O_4$ catalysts was performed in a fixed-bed tubular reactor at atmospheric pressure with 0.1 g catalyst. Prior to the CL-CDR looping reaction, 10%H_2 balanced with N_2 was fed into the reactor at 800 ^oC for 2 h to reduce the catalyst. In the methane decomposition step, a flow of 30 cc/mim feed gas containing 5%CH_4/N_2 passed through for 30mins at 700 ^oC. After using N_2 to purge the feed gas in the last step, 20%CO_2 balanced with N_2 flowed through the catalysts to carry out the reverse boudouard CO_2 reaction for 15 minutes at 700 ^oC.

Results and discussion.

The activity of Ni -Co/$MgAl_2O_4$ maintained even after 20 cycles of CL-CDR process as shown in **Figure 1**. Spinel-type $MgAl_2O_4$ has positive effects on conversion on the catalyst surfaces, which affected the ratio of H_2 to CO and H_2 purity during methane decomposition step as well.

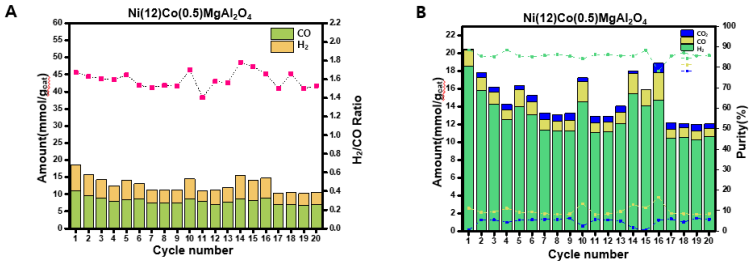

Figure 1. (A) H_2 and CO yield within 20 cycles, (B) Purity of products formed by CH_4 decomposition.

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Cu-Mn substitution in spinel ferrites orients the mechanism of chemical-loop reforming of ethanol

Olena Vozniuk[1,2], Thomas Cacciaguerra[1], Nathalie Tanchoux[1], Stefania Albonetti[2], Lorenzo Stievano[1], Jean-Marc M. Millet[3], Nicolas Bion[4], Francesco Di Renzo[1*], Fabrizio Cavani[2]

[1] *ICGM, University of Montpellier-CNRS-ENSCM*
[2] *Dip. Chimica Industriale "Toso Montanari", Alma Mater Studiorum Università di Bologna*
[3] *IRCELYON, University Lyon-1, France*
[4] *IC2MP, University of Poitiers-CNRS, France*
[*] *francesco.di-renzo@umontpellier.fr*

Introduction. In a chemical loop process, a solid oxygen carrier (SOC) is reduced and oxidized in successive steps: in the reducing step, the SOC lends oxygen to an electron acceptor; in the oxidizing step, the SOC is reoxidized by water steam, releasing hydrogen. This process is currently used in hydrogen storage cycles, in which hydrogen is used as a reducer and is released back by steam when required. The use of ethanol as a reducer allows to produce hydrogen from renewable biomass. Transition metal-doped iron oxides are effective SOC materials, as the reducing and oxidizing steps can be easily performed at the same temperature [1]. The nature of the transition metal heavily affects the pattern of reduction of ferrite by ethanol in the first step of the chemical loop [2,3].

Experimental/methodology. SOC materials have been prepared by precipitation in alkaline solution and calcination. They have been characterized by XRD, Raman and Mössbauer spectroscopy, H_2-TPR, ^{16}O-^{18}O exchange, N2 sorption. Redox cycles were carried out at 450°C in a flow reactor with alternate feed of ethanol and water vapor. Products of ethanol oxidation and SOC reoxidation were quantitatively analysed.

Results and discussion. In the reduction of copper ferrite, early formation of Cu^0 catalyzes ethanol reforming with the formation of CO and fast reduction of the spinel to iron carbides FeC_x (Fig. 1). Manganese ferrite catalyzes ethanol oxydehydrogenation and is more slowly reduced to maganowustite (Mn,Fe)O. In the reoxidation step of the chemical loop, the deeper reduction of the Cu-bearing SOC allows a higher H_2 production but the oxidation of iron carbides develops COx, which affect the purity of the produced hydrogen, in a trade-off between conversion and selectivity.

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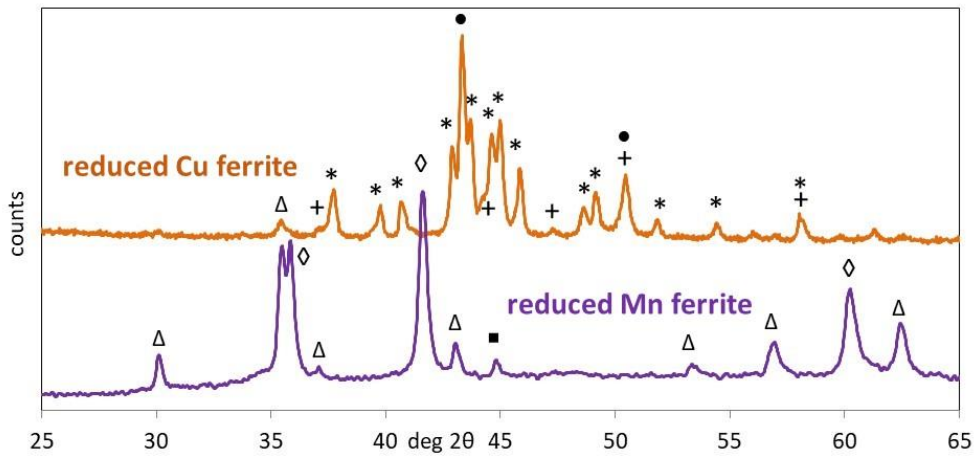

Fig. 1 – XRD patterns of $Cu_{0.6}Fe_{2.4}O_4$ (top) and $Mn_{0.6}Fe_{2.4}O4$ (bottom) reduced by ethanol vapor. Main peaks: spinel (Δ), copper (●), Fe_2C_5 (+), FeC_3 (*), wustite (◊), α-Fe (■)

Short pulse reductive activation of Pt/ceria for the low-temperature CO abatement in vehicles operated with the synthetic Diesel fuel OME

D. Eisenbeil[1,2], P. Demel[1], M. Haas[2], H. Hamel[1], B. Betz[2], A. Dreizler[1], C. Beidl[1], M. Votsmeier[1,2,]*

[1]Technische Universität Darmstadt, Alarich-Weiss-Straße 8, 64287 Darmstadt, Germany
[2]Umicore AG & Co. KG, Rodenbacher Chaussee 4, 63457 Hanau, Germany
**martin.votsmeier@eu.umicore.com*

Keywords: Pt/ceria, Short Puls Activation, OME.

Introduction

In previous work, we have shown that after activation by 5-10 s long reductive pulses, Pt/ceria catalysts can achieve very high CO oxidation activity at temperatures as low as 70°C [1]. However, under conventional Diesel exhaust ageing conditions (~800°C in lean exhaust), Pt/ceria catalysts deactivate through the formation of inactive Pt single atoms [2]. This deactivation requires a complicated 2-step activation procedure [1] that makes a practical application of these catalysts for Diesel exhaust after treatment difficult. Due to the lower ageing temperatures during operation with Oxymethylene Ether (OME) as an alternative Diesel fuel, Pt will not form single atoms, which greatly simplifies the application of the short pulse activation scheme. In this contribution, we demonstrate the application of short-pulse reductive activation of Pt/ceria catalysts for OME exhaust with a focus on CO abatement.

Experimental/methodology

Exhaust temperature profiles, mass flows, and raw emissions of a low-load cold-start driving cycle were measured on an engine bench and then reproduced on a dynamic lab test bench. A Pt/ceria catalyst was prepared by incipient wetness impregnation using commercial high-surface ceria (BET 140 m^2/g). The catalytic material was then coated on a cordierite monolith.

Results and discussion

To demonstrate the performance of Pt/ceria catalyst after short pulse activation, a sequence of drive cycles was measured on the dynamic test bench. In between the cycles, the catalyst was activated by a 10 s reductive pulse at 230°C, see Fig. 1 for the applied test sequence. The performance in the different cycles is compared with the performance of a commercial reference Diesel oxidation catalyst (DOC) in the same cycle. With the Pt/ceria catalyst, after each activation event nearly full CO conversion could be measured in the following drive cycle (Fig. 1: 2.DC, 5.DC and 9.DC). Without further activation, the activity slowly decreases from drive cycle to drive cycle but is restored with each new regeneration. After a deactivation step at 450°C mimicking full operation of the OME engine, the activation is completely lost but can be regained by a new activation pulse. [3].

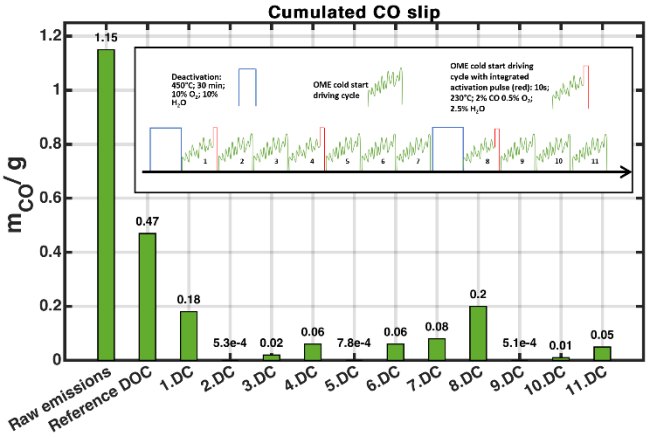

Figure 1. Comparison of the cumulated post-catalyst CO mass for the 30-minute OME cold-start driving cycle (DC) in the Pt/ceria test series: 1. DC - 11. DC. The cumulated mass of the raw emissions and the test with a reference DOC are provided for comparison.

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Methanation catalysts under dynamic reaction conditions: Spatially and temporally resolved reaction data and modelling

T. Engl[1*], D. Kellermann[2], M. Langer[2], H. Freund[2], M. Rubin[1], R. Dittmeyer[1]

[1]*Institute for Micro Reaction Engineering (IMVT), Karlsruhe Institute of Technology (KIT), Germany*
[2]*Institute of Reaction Engineering and Catalysis, Technische Universität Dortmund (TUDO), Germany*
[*]*timo.engl@kit.edu*

Introduction

In order to limit the negative effect of climate change, the transition of the energy system from fossil to sustainable and climate neutral energy sources and energy carriers is a major challenge. However, since renewable energies (RE) such as wind and solar power are not equally available at all times and in all places, the storage and distribution of RE are of great importance. In this context, power-to-X technologies producing chemical energy carriers will be one piece of the puzzle. In particular, the methanation reaction is an important synthesis route, since it is already well investigated and can rather easily be implemented in the existing natural gas infrastrucutre. However, due to temporal fluctuations of the RE, a dynamic operation of the reaction is necessary when larger buffer tanks are to be avoided. This raises questions on the operation conditions, respectively on the effects of dynamic operation on potential deactivation of the catalyst applied. In the frame of the priority programm 2080 funded by the German Research Foundation, the methanation reaction is investigated under dynamic and deactivating conditions with focus on catalyst stability and deactivation phenomena.

Experimental/methodology

The CO_2 methanation reaction was investigated using an in-house developed reactor with multiple taps along the reaction coordinate (Fig. 1a), allowing for spatially and temporally resolved gas phase sampling in between dedicated reaction zones realized by implementing individual foils coated with the catalyst. The reactor further allows for optical access which will be used to gather data on adsorbed species on the catalyst's surface via DRIFTS, giving insights into the reaction mechanism on the catalyst's surface. From the extensive data obtained at different temperatures, feed gas composition (step changes), etc., information on catalyst stability under dynamic reaction conditions is deduced.

Results and discussion

Exemplarily, Fig. 1b shows the spatially resolved CO_2-conversion profile of the methanation reaction obtained at different reaction temperatures using an industrial methanation reference catalyst (IMRC). In the contribution, we will present and discuss spatial and temporal profiles of the methanation reaction under certain (dynamic) reaction conditions. Additionally, a modell for catalyst deactivation has been developed and will be compared with the data collected with the tap reactor.

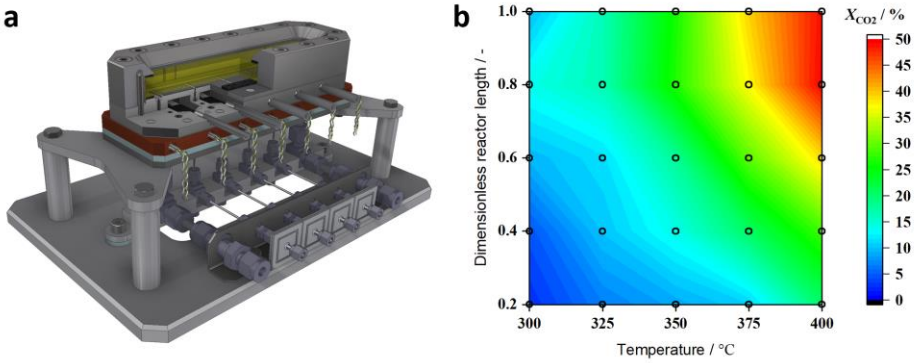

Figure 1: (a) CAD drawing of the reactor used to gather temporally and spacially resolve operando data. (b) Spatially resolved CO2 conversion at different T_R (p_R = 5 bar, SV = 4 $ml_N\ min^{-1}\ mg_{cat}^{-1}$, CO_2:H_2 = 1:4 with 50 vol.% N_2). Heat map shows the interpolation of the 5x5 experimental points indicated by circles).

Acknowledgments: *The Authors acknowledge the funding by the German Research Foundation (DFG priority program 2080 ''Catalysts and reactors under dynamic conditions for energy storage and conversion'').*

CO_2 hydrogenation over potassium promoted Fe/YZrO$_x$: Operando DRIFTS analysis of mechanistic aspects.

E. Fedorova[1*], J. Weiß[1], L. Kraußer[1], C. Kubis[1], E. Kondratenko[1], A. Brückner[1]

[1]*Leibniz-Institut für Katalyse e.V., Rostock, Germany*
[*]*elizaveta.fedorova@catalysis.de*

Introduction. CO_2 hydrogenation to higher hydrocarbons via consecutive RWGS and Fischer-Tropsch synthesis is one promising approach to utilize CO_2 greenhouse gas into valuable chemicals and fuels. Iron based catalysts are well known to be widely used for this prosses. Using potassium as promoter is especially necessary to increase selectivity of C_{2+} hydrocarbons and suppress methane formation. Even though iron-based catalysts have been studied for a long time, there are still open aspects regarding the mechanistic details. For this purpose, *operando* DRIFT spectroscopy studies under high pressure with MS analysis were performed on unpromoted and potassium promoted Fe/YZrO$_x$ catalysts.

Experimental/methodology.

Fe/YZrOx catalysts promoted by potassium was synthesized by incipient wetness impregnation method. The operando DRIFTS experiments were performed on a Nicolet iS10 spectrometer equipped with a high pressure/high temperature reaction DRIFTS cell (Harrick) connected to a gas supplying system and to an online mass spectrometer (OmniStar GSD320, Pfeiffer Vacuum). The catalysts were pretreated in H_2 (H_2/He, 1:1, 400°C, 120 min) followed by exposure to the reaction gas mixture (CO_2/H_2, 1/3, 15 bar, 300°C). In addition, the catalysts were studied by the sequential treatments in reaction gases: CO_2→He→H_2, CO_2→H_2 and H_2→CO_2 with 22% of CO_2 in He and 5% of H_2 in He.

Results and discussion. The DRIFT spectra of 1K-Fe/YZrOx recorded under different sequences of treatments are depicted in Fig.1. The surface of the catalyst after flushing in CO_2 is characterized by several carbonate and bicarbonate adsorbates with different structures[1]. After He treatment, a vanishing of ~~a~~ weakly adsorbed carbonates is observed. Further H_2 dosing leads to the transformation of surface carbonates only into CH_4 and C_{2+} hydrocarbons. This could be an indication to a direct reaction route on the stable sites presented on the surface after treatment in He. Indeed, the direct addition of H_2 after CO_2 seems to lead to the formation of CO primarily from weakly adsorbed carbonates by RWGS reaction and further formation of methane from stronger adsorbed carbonates. Further studies are currently underway to validate this assumption.

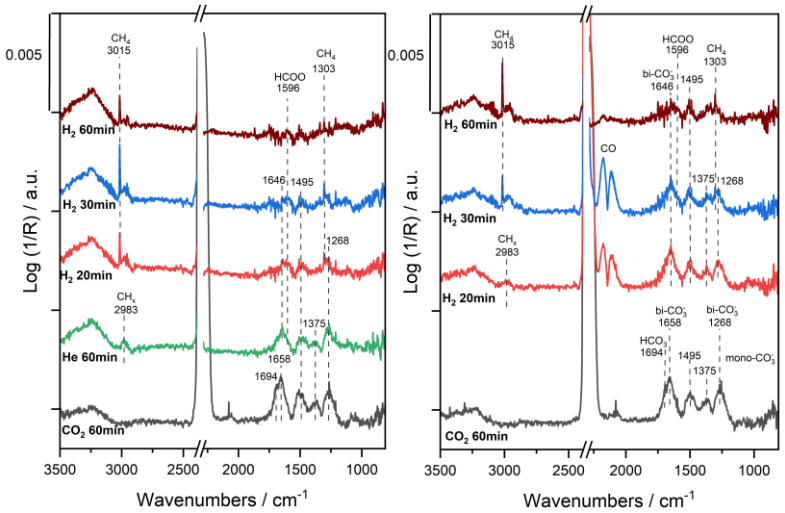

Figure 1. DRIFT spectra of 1K-Fe/YZrOx catalyst measured under sequential exposure to CO_2→He→H_2 (left) and to CO_2→H_2 (right) at 15 bar and 300°C.

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Effects of support acidity of noble and transition metal catalysts on the dehydrogenation of Methylcyclohexane

P. Fernandez[1], E. Farah[1], E. Kantarelis[1*]

[1]*KTH Royal Institute of Technology, Stockholm, Sweden*
[*]*ekan@kth.se*

Keywords: LOHC, hydrogen, dehydrogenation, surface acidity

Introduction. The current climate strategy urges to limit the use of fossil resources and increase the share of renewable energy and hence green H_2 is contemplated as a promising alternative. However, it exhibits a low volumetric energy density and thus its storage and delivery represent a major bottleneck. Chemical fixation of H_2 in liquid organic molecules-carriers (LOHC) undergoing cyclic hydrogenation-dehydrogenation reactions is a promising alternative. Nevertheless, existing catalysts are not fully optimized to allow the technology to reach its full potential[1]. The acidity of the support in the gas phase dehydrogenation of methylcyclohexane (MCH) has been identified as an important factor for affecting side reactions and more importantly the C-C scission[2]. In view of this, the present study extends to MCH dehydrogenation on a bimetallic -noble (Pt) and transition metal (Ni) catalysts supported on supports of different acidity. The effect of acidity on promoting the C-H scission selectivity is investigated together with anchoring as well as spillover phenomena with a focus on the long-term stability of the catalysts.

Experimental/methodology. The gas phase catalytic dehydrogenation of MCH is studied in a fixed bed reactor at a temperature range of 250 - 400 °C and atmospheric pressure (Fig1.). Conventional γ-Al_2O_3 was used as typical acidic support, while $MgAl_2O_4$ as non-acidic one and was synthesized according to the co-precipitation method. Pt and Ni were chosen as the noble and transition metals respectively. The MCH was co-fed to the reactor with N_2 at a 5:1 ratio. H_2 and other gaseous products were quantified using online GC-FID/TCD, while liquid samples were also analyzed offline to determine the selectivity towards toluene.

Results and discussion. NH_3 TPD experiments (Fig 2) indicate that γ-Al_2O_3 exhibits surface acidity as opposed to $MgAl_2O_4$ affecting metal dispersion and secondary reactions. Detailed experimental investigation is ongoing.

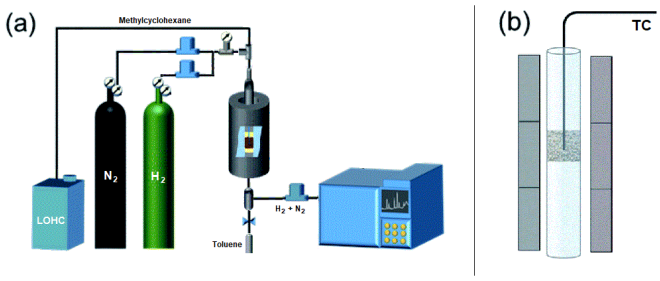

Figure 1a) Experimental set up b) catalytic fixed bed detail

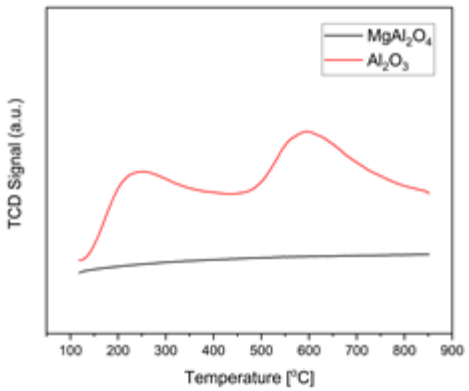

Figure 2. Acidity expressed by NH_3-TPD for supports

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Effect of H/N ratio control in a multi-bed ammonia synthesis reactor using a Ru-based catalyst

Y. Goto[1*], M. Kikugawa[1], K. Yamazaki[1], Y. Manaka[2], T. Nanba[2], H. Matsumoto[2,3], S. Ookawara[3], A. Sato[4], M. Aoki[1], N. Baba[1]

[1]*Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan*
[2]*National Institute of Advanced Industrial Science and Technology, Koriyama, Fukushima, Japan*
[3]*Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan*
[4]*Toyota Motor Corporation, Susono, Shizuoka, Japan*
[*]*E-mail: yoshihiro-goto@mosk.tytlabs.co.jp*

Introduction

Ammonia (NH_3), an essential raw material for agricultural fertilizers and synthetic chemicals, has recently attracted attention owing to its applicability as a hydrogen carrier or fuel [1]. Industrial NH_3 synthesis is performed by the well-known Haber–Bosch process using Fe-based catalysts, which require harsh reaction conditions (20–30 MPa); thus, the development of both catalysts and reaction systems that allow the synthesis of NH_3 under mild conditions is desired to increase the use of NH_3. Although Ru supported on rare earth oxides (e.g., $Ru/Ce_{0.5}La_{0.4}Ti_{0.1}O_{1.8}$) [2] are promising catalysts for achieving this goal, Ru catalysts generally suffer from hydrogen poisoning, which inhibits the NH_3 synthesis at a high H_2 partial pressure in the reaction gas. The optimal H/N ratio of the reaction gas may depend on the reaction temperature owing to the effects of the hydrogen poisoning and the equilibrium concentration of NH_3. Thus, in a multi-bed NH_3 synthesis reactor that is typically adopted in industrial plants, controlling the H/N ratio for each catalyst bed at different temperatures can potentially improve the NH_3 productivity of the reaction system.

Results and discussion

In this study, first, the H/N-ratio-dependence of the NH_3 synthesis activity of the developed Ru catalyst, $Ru(5\ wt\%)/Ce_{0.5}La_{0.4}Si_{0.1}O_{1.8}$, under isothermal conditions was investigated using a fixed-bed reactor. The H/N ratio at which the catalyst exhibited the highest activity shifted toward a lower value at a lower temperature, indicating that the suitable H/N ratio for achieving the optimal activity of the catalyst in NH_3 synthesis decreases with decreasing reaction temperature (Fig. 1a). Further, a prototype of a double-bed NH_3 reactor (Bed 1: high temperature, Bed 2: low temperature) was constructed to investigate the effect of the control of the H/N ratio for each catalyst bed (Fig. 1b). This control was achieved by the split supply of the feed gas to Bed 2. The NH_3 productivity increased as the H/N ratio of Bed 2 decreased with the split supply (Fig. 1c), suggesting that an appropriate control of the H/N ratio in Bed 2 against that of Bed 1 can improve the overall NH_3 productivity. Furthermore, the steady-state operation of the double-bed reactor with the recycling of the unreacted gas was also successfully achieved.

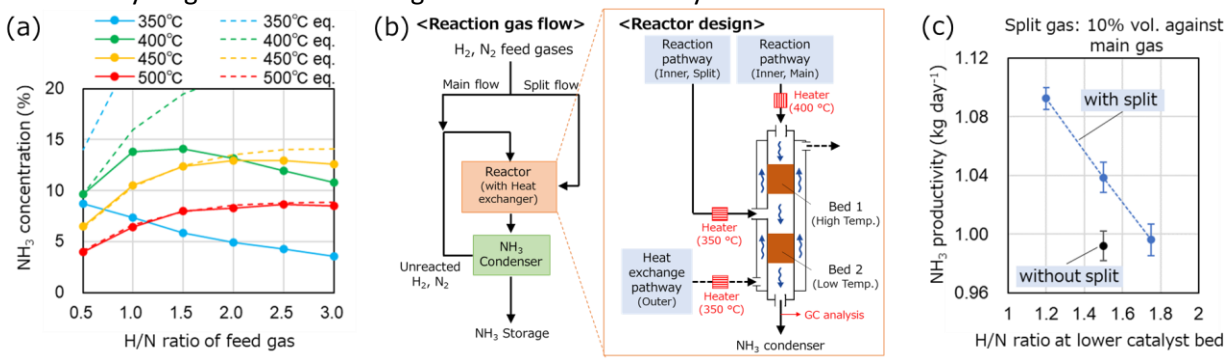

Figure 1. (a) H/N-ratio-dependence of NH_3 production on $Ru/Ce_{0.5}La_{0.4}Si_{0.1}O_{1.8}$ (catalyst, 1 mL; flow rate, 185 mL min^{-1}; pressure, 8 MPa). (b) Simplified gas flowsheet for a double-bed reactor. (c) Effect of the split supply of H_2/N_2 gas on NH_3 productivity (catalyst, 20 mL for each bed; reaction gas, H/N = 1.5 with a flow rate of 7.4 L min^{-1}; pressure, 8 MPa). The split supply gas of 0–100% H_2/N_2 (0.74 L min^{-1}) was introduced into Bed 2 to control the H/N ratio at 1.20–1.75.

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Operando X-ray absorption spectroscopy as a first step towards a knowledge-based optimization of Fischer-Tropsch catalysts

R. Elbuga-Ilica[1,2], A. Zimina[1,2], M.-A. Serrer[1,2], E. Saraçi[1,2], J.-D. Grunwaldt[1,2]

[1]*KIT/IKFT Eggenstein-Leopoldshafen,Karlsruhe,Germany*
[2]*KIT/ITCP, Karlsruhe, Germany*
* Corresponding authors: *anna.zimina@kit.edu; erisa.saraci@kit.edu*

Introduction

Power-to-liquid processes can be considered the key for renewable electricity-based liquid fuel generation. [1,2] For this purpose, H_2 generated *via* water electrolysis and CO_2 provided *via* "carbon capture" are converted together on a suitable catalysts [3] and hydrocarbons, various olefins and methanol can be synthesized via Fischer-Tropsch process (FTS)[2]. For catalyst improvement, *in-situ* and *operando* characterization of FTS catalysts is considered essential to derive structure-activity relationships. [4] In this respect, *operando* X-ray absorption spectroscopy (XAS) can be used to observe structural changes of active sites of heterogeneous catalysts at work. The study is of significant importance, mainly in view of growing demand for energy storage using CO_2 as feedstock and renewable electrical energy.[5] For this purposes, a dedicated *operando* reactor system has been recently developed at the CAT-ACT beamline at KIT Light Source [6] that allows an operation close to the industrially relevant FTS conditions [4].

Results and discussion

The high-pressure and high-temperature setup was developed in-house [5] and installed at the CAT-ACT beamline.[6] As a pilot study, commercially representative Co-Ni-Re/γ-Al_2O_3-FTS-catalysts were investigated at 250°C and 30 bar for more than 300h. The products were investigated by online μ-GC and offline GC-FID to trace the catalytic activity and selectivity. The study showed that considering the high stability of the catalysts, the main reason of catalyst deactivation is due to macroscopic effects such as pore blocking by reaction products and diffusion limitation. The formation of carbon species was confirmed from XAS analysis and investigated by complementary characterization methods, such as Raman spectroscopy, TPH, and TPO. It was found that the formation of atomic carbon, surface carbides, hydrocarbons, graphitic carbon deposits and hydrogen resistant carbon species, led to increased limitation of pore diffusion. Based on this obtained information, we aim to prepare a model FTS catalyst and further optimize it for improved activity and selectivity. For the synthesis of model catalysts, different methods like wet-impregnation, co-precipitation, flame spray pyrolysis etc. are used. Considering different atomic structures produced by different methods, the structure-activity relation is explored in detail, including the metal-support interaction and the role of promoters using *operando* spectroscopy. Part of the findings, will support new energy-related initiatives in Germany, like the Care-o-Sene project [7], a research collaborations focused on the production of sustainable aviation fuel.

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Additively manufactured reactor development for exothermic synthesis

Niko Heikkinen*, Christian Frilund, Niko Virkki, Pekka Simell, Matti Reinikainen, Antti Pasanen

VTT Technical Research Centre of Finland, Espoo, Finland

Keywords: Additive manufacturing, metallic 3D printing, Fischer-Tropsch synthesis

Current chemical industry is in a phase of transition from fossil raw materials to renewable feedstocks. In order to create feasible synthesis routes for varying renewable feedstocks, novel reactor solutions are required. We present the design and testing of a heat exchanger type reactor, suitable for many exothermic synthesis reactions, such as Fischer-Tropsch and methanol synthesis and methanation. Our approach was to prepare the reactor with metal additive manufacturing (AM) to gain simplification, and most importantly, improved design freedoms over the traditional manufacturing methods of these types of devices. The basic design was inspired by cross-flow heat exchangers, often used in microfluidics, having multiple distinct channels for both the hot fluid and cold fluid side. Cross-flow heat exchangers, can be manufactured by for example diffusion bonding, vacuum soldering and laser welding where etched metal plates are co-joined together to form the channel networks [1].

The laboratory scale unit was designed to meet the requirement for high pressure (up to 30 bar) and moderate temperatures (up to 400 °C). It features a cylindrical channel geometry where the 1.5 mm i.d. catalyst (i.e. gas) filled channels have a 5 mm centre-to-centre distance from each other with a total of 20 catalyst channels of 75 mm height (72 mm actively cooled height). The reactor body features flange surfaces at both ends of the gas channels. This, combined with the straightforward catalyst channel geometry, allows for easy full access to the catalyst channels for convenient particulate catalyst filling and removal. The reactor body also featured integrated pockets for cartridge heaters.

The continuous Fischer-Tropsch experiments were performed at a temperature of 209 – 229 °C, pressure of 20 bar and a H_2/CO ratio of 2. The reactor was packed with a catalyst bed of 3.34 gram and reduced at 400 °C with H_2 (100 cm_3 STP min^{-1} $gcat^{-1}$) for 16 h. In total, five different reaction conditions (from A to E) were tested during the ~390 h time-on-stream. Table 1 presents the reaction setpoint temperature, gas flows, results for CO conversion and selectivity. Especially interesting value is the CH4 selectivity. In a presence of local hotspots in the catalyst bed, typically the CH4 selectivity will be increased. In parallel to the 3D printed reactor development, the same Co-Pt-Si/γ-Al_2O_3 catalyst was tested in a traditional tubular reactor without active reaction heat removal. In these experiments, the CH4 selectivity ranged between 16 - 18 m-% at a CO conversion level of ~15 %.

Table 1, A reaction condition summary for each reaction setpoint. Pressure was fixed to 20 bar_a in all steps.

Reaction setpoint	Temperature [°C]	Total inlet gas flow [nL h^{-1}]	Gas hourly space velocity [nL g_{cat}^{-1} h^{-1}]	CO conversion [%]	Wax ASF-α [-]	CH_4 selectivity [m-%]	C_{5+} selectivity [m-%]	O/P ratio (C_2-C_4) [-]
A	209	18	5.4	16	-	-	-	-
B	209	12	3.6	25	-	-	-	-
C	209	6	1.8	49	0.880	9.2	82.8	0.92
D	229	18	5.4	61	-	-	-	-
E	229	12	3.6	76	0.878	10.8	80.7	1.79

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X-Ray Operando Studies of Catalytic Dehydrogenation in LOHC Technology

O. Irrazábal [1], O.M. Magnussen[2], C. Paetz[3], K. Lomachenko[1], A. Sartori[1], J. Frey[1] and J. Drnec[1]

[1]*European Synchrotron Radiation Facility (ESRF), 39000 Grenoble (France).*
[2]*Institute of Experimental and Applied Physics (IEAP) - CAU, 24118 Kiel (Germany).*
[3]*Hydrogenious LOHC Technology GmbH, 91058 Erlangen (Germany).*

Keywords: LOHC, hydrogen, energy storage, operando, XRD, XAS, catalysis, reactor, single crystal.

Introduction. Liquid organic hydrogen carriers (LOHC) represent a promising alternative for the storage and transportation of hydrogen [1,2], enabling high H_2 storage densities in a liquid at ambient conditions [3]. In order to make this truly cyclic, a high catalyst stability at the dehydrogenation reaction is necessary.

Experimental/methodology. We are studying the dehydrogenation reaction of liquid benzyltoluene at its interphase with solid Pt catalysts. For this, we use high energy X-Ray diffraction (HEXRD) and X-Ray absorption spectroscopy (XAS) to study the reaction in operando under realistic conditions (300 °C, 1-5 bar). These measurements provide atomic-scale insights on the degradation processes of the catalyst during the reaction. We perform these measurements at the ID31 and BM23 beamlines of the European Synchrotron Radiation Facility (ESRF).

Results and discussion. In this presentation we will report on the design of a suitable semi-industrial reactor for the operando HEXRD studies, adapted for both model and commercial catalysts. We also describe strategies to optimize the catalyst and diffraction geometry to avoid background scattering and stability problems that arise when studying HEXRD on such commercial scale systems, and discuss about the representativeness of model catalysts for these studies.

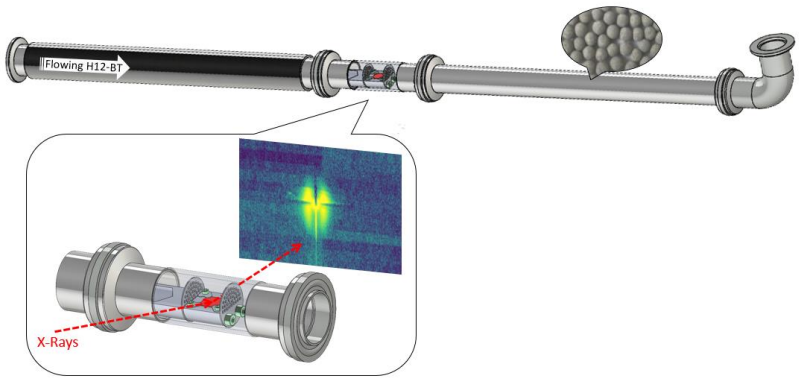

Image 1. Semi-industrial reactor for LOHC dehydrogenation suitable for operando HEXRD studies.

Furthermore, we will present the first results from operando HEXRD measurements at ID31, where we can follow the changes of the nanoparticles and their lattice parameter along the reaction.
We will also present the design of a model cell adapted to study the reaction at small scale with XAS on commercial catalysts, and show the first results acquired with this technique, that shed light onto the changing chemistry of the catalyst.

Acknowledgments
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Use of a newly developed reactor concept: Reverse water-gas shift reaction at ambient pressure

Dimitrij Ješić[a], Andrej Pohar[a], Blaž Likozar[a]*
[a]National Institute of Chemistry, Hajdrihova 19, 1001 Ljubljana, Slovenia
**Corresponding author: Dimitrij Ješić Dimitrij.jesic@ki.si*

Key words: Reactor design, Multiscale modeling, Mass transfer, Rotating fixed bed, Reaction kinetics, RWGS

Converting CO_2 into fuels and chemicals is an important step in mitigating the negative environmental impacts of CO_2 emissions. Direct use of CO_2 is still in its infancy, and syngas, mostly from coal gasification, remains the main source of CO and hydrogen for the chemical industry. Direct production of methanol and dimethyl ether from CO_2 is difficult due to low yields and unfavorable thermodynamic conditions. The catalytic reverse water-gas shift reaction (RWGS) offers a promising solution for the conversion of CO_2 into fuels. Metal-based catalysts have been developed to improve the efficiency, CO selectivity, and stability of the reaction, with recent advances in catalyst design and a deeper understanding of the reaction mechanism leading to improved catalysts. However, catalyst stability at high temperatures needs further improvement, and the active sites of the reaction remain controversial. Two main mechanisms for the RWGS reaction have been proposed in the literature: the redox mechanism and the formate mechanism.

The XMTE (external mass transfer eliminator) reactor, specifically designed to perform experiments without mass transfer limitations, is highlighted as a key component of the proposed process. This allows accurate determination of microkinetic mechanisms and reaction kinetics, which is critical for developing a microkinetic model and determining kinetic parameters. The reactor design is also discussed as a major improvement over conventional CSTR reactors, as it mitigates the weaknesses of these systems and allows for optimal operation.

In addition to the development of the process and reactor design, the work presented includes the exploration of the RWGS reaction at ambient pressure with the proposed HiFUEL W230 catalyst as a starting point for further research on more complex conversions such as oxidative methane coupling. The results should provide insight into the potential for increasing syngas to fuel production and efficiency, as well as the economics of the process. Overall, XMTE highlights the potential of the proposed process and reactor design to address the global chemical to fuel shortage and improve production efficiency.

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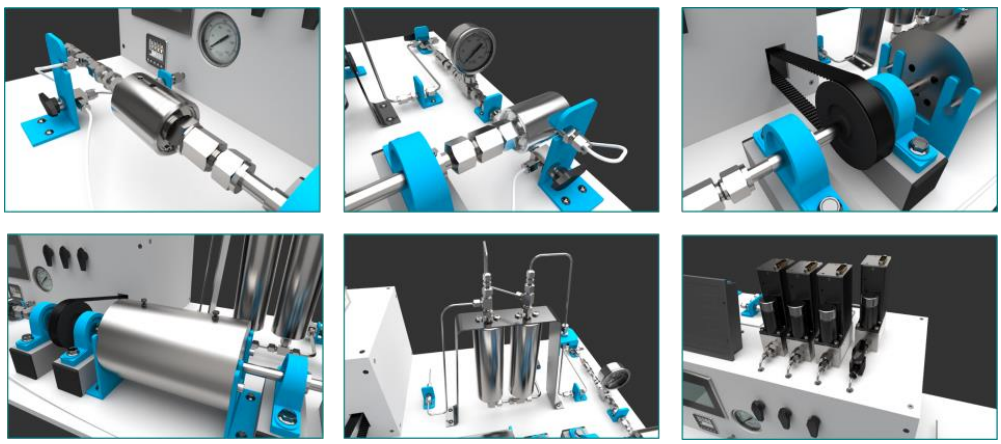

Ammonia decomposition over Ru/Al@Al_2O_3 Catalysts

Ho Jin Lee[1], Eun Duck Park[1,2*]

[1]*Department of Energy Systems Research, Ajou University, Suwon 16499, Korea*
[2]*Department of Chemical Engineering, Ajou University, Suwon 16499, Korea*
*****edpark@ajou.ac.kr*

Keywords: NH_3 decomposition, Hydrogen production, Ru/Al@Al_2O_3, Core-shell

Introduction. Because of climate change resulted form CO_2 emissions, the transition from a carbon economy society to a hydrogen economy one is drawing attention. NH_3 is a promising hydrogen carrier for its high gravimetric (17.8 wt.% H_2) and volumetric (121 kg/m^3 in the liquid form) H_2 density. Hydrogen production through NH_3 decomposition reaction occurs at high temperature (> 450 °C) and requires a lot of energy. Therefore, it is required to develop a catalyst for efficiently producing hydrogen at low temperatures. A broad range of metals have been tested for NH_3 decomposition, such as Ru, Ni, Rh, Co, Fe, Pt, and Pd. Among them, Ru has been the most active and stable metal. In addition to active metals, the importance of the catalyst support in the supported catalyst can be emphasized because the support stabilizes the active sites not to be deactivated through sintering and agglomeration. The surface area, mechanical and thermal properties of a support are additional factors that have a significant impact on catalyst performance. Especially, the thermal conductivity of the catalyst support can affect the catalytic performance for the highly exothermic and endothermic reaction. In the Al@Al_2O_3 core-shell, the Al core is desirable to guarantee the facilitated heat flux and the Al_2O_3 layer is essential to stabilize the Ru metal against sintering and agglomeration under reaction conditions.

In this study, we prepared various Ru/Al@Al_2O_3 catalysts with different Al contents by changing the reaction time during wet impregnation method. Then, we applied them to NH_3 decomposition reaction and found that the NH_3 decomposition activity was dependent on the Al content in the Ru/Al@Al_2O_3 catalysts.

Experimental/methodology. The activity of the NH_3 decomposition reaction was evaluated in a packed-bed reactor at atmospheric pressure. In general, catalyst powder of 100 mg was loaded in the middle of a quartz reactor (O.D. = 9.525 mm, I.D. = 7.745 mm) and retained by quartz wool. Before the activity test, the prepared catalyst sample was first reduced with pure H_2 gas at a flow rate of 30 mL/min at 350 °C, if not specified, for 1 h, followed by cooling to 25 °C. H_2 gas was then switched with He gas to purge the residual hydrogen at a flow rate of 30 mL/min for 30 min. Then, the feed gas, which was composed of 25 mol% NH_3, 70 mol% He, and 5 mol% CH_4, was fed into the reactor at a total flow rate of 100 mL/min. CH_4 was used as an internal standard. The catalytic activity for NH_3 decomposition was monitored by increasing the temperature from 300 to 600 °C under atmospheric pressure. The reactants and products were separated using a Porapak Q column and analyzed using a thermal conductivity detector (TCD) in a gas chromatograph.

Results and discussion. Catalytic activity for NH_3 decomposition was evaluated for Ru/Al@Al_2O_3 catalysts. NH_3 conversions as a function of the reaction temperature over different catalysts are shown in Fig. 1. The NH_3 conversion at 400 °C decreased in the following order: Ru/Al@Al_2O_3(0h) > Ru/Al@Al_2O_3(1h) > Ru/Al@Al_2O_3(2h) > Ru/Al@Al_2O_3(4h) > Ru/Al@Al_2O_3(6h). This implied that the catalytic activity was dependent on the Al content in the Al@Al_2O_3.

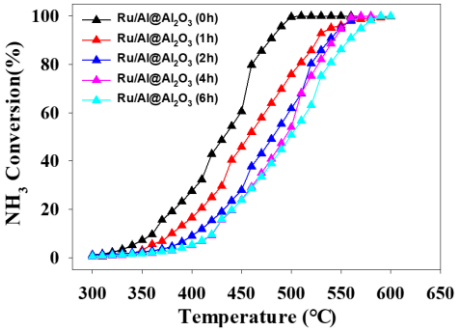

Figure 1 NH_3 decomposition for NH_3 decomposition over Ru catalysts. Reaction conditions: feed composition (25 mol% NH_3, 70 mol% He, and 5 mol% CH_4), WHSV = 60,000 mL/g_{cat}/h.

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Pair Distribution Function for local restructuring phenomena in γ-Al_2O_3 supports and active catalyst particles

F. Manzoni[1*], S. Schlicher[2], M. Bauer[2], M. Zobel[1]

[1] *Institute of Crystallography, RWTH Aachen University, Aachen, Germany;*
[2]*Department of Chemistry and Center for Sustainable Systems Design (CSSD), Paderborn University, Paderborn, Germany;*
[*]*manzoni@ifk.rwth-aachen.de*

Introduction.
Supported catalysts feature a complex interplay of local disorder and defect structures: small metal clusters, phase transformations of active species, nanoparticle-support interactions creating additional interfacial phases, as well as defective aluminum oxide supports. To adress this plethora of structural motifs, we employ total scattering. While X-ray absorption spectroscopy can element-specifically analyse few coordination shells and short-range order, Pair Distribution Function (PDF) analysis of high-energy X-ray scattering data can access disorder and structure on lengthscales from ~ 1 Å to several tenths of nanometers.

Experimental/methodology.
The PDF is a histogram of all interatomic distances in the sample, from which we can evaluate cluster and nanoparticle sizes and structures, local and possibly thermal disorder, as well as support restructuring. In order to achieve ultimate insight into the supported species or the support only, difference-PDFs (d-PDF) are calculated. For this, the total scattering of an unloaded supported is subtracted from the catalyst, both measured at reaction conditions, typically in transmission mode in a glass capillary. We have pushed laboratory PDF to achieve such insight on ex-situ samples [1,2], complementing sub(second) resolution for operando studies at synchrotron sources.

Results and discussion.
Here, we show how to access both the structure of active species (Fig. 1a) and the Al_2O_3 support (Fig. 1b). The d-PDF refinement in Fig. 1a highlights the sensitivity of the PDF technique to identify the co-existence of Fe_2O_3 clusters of only 1 nm diameter next to larger γ-Fe_2O_3 nanoparticles on an Al_2O_3 support - impossible to detect in common X-ray diffraction data, but well in line with XAS results for the cluster species. [2] The defective short-range order of the Al_2O_3 support of this study as well as the one of common CO_2 methanation catalysts such as Ni@γ-Al_2O_3 can further be characterized via PDF analysis. Despite a recently improved structural model for γ-Al_2O_3 by Paglia et al.[3], based on an improved tetragonal structure with defective oxygen sublattice, this model is insufficient to accurately describe the short-range order < 10 Å, see Fig. 1b. We address these deficiencies, which become particularly important when small changes of nanoparticle-support interactions of Ni@Al_2O_3 methanation catalysts are followed operando to derive structure-activity relationships for in-situ PDF measurements at P02.1 beamline, PETRA III.

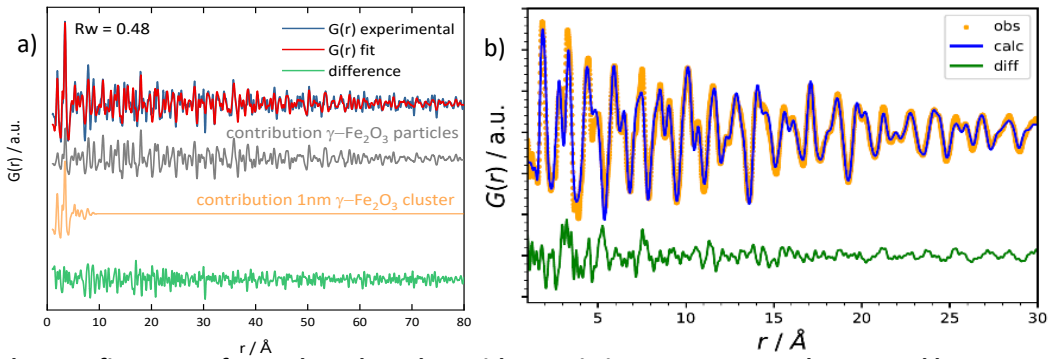

Fig1: a) d-PDF refinement of an Fe based catalyst with co-existing γ-Fe_2O_3 1 nm clusters and larger particles. b) Local restructuring in γ-Al_2O_3

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Comprehensive reverse flow reactor model for fluid-solid systems

Luca Mastroianni[1,2], Martino Di Serio[1], Tapio Salmi[2], Vincenzo Russo[1,2]

[1]*Università degli Studi di Napoli Federico II, Department of Chemical Sciences, Napoli, Italy*
[2] *Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Turku, Finland*
[*]*v.russo@unina.it*

Introduction. The minimization of the energy supply to conduct chemical transformations is one of the fundamental ideologies of process intensification and it is of crucial importance in the journey towards a greener chemical industry. For exothermic processes, packed bed reactors with periodic flow reversal, i.e., reactors in which the feed is switched between the two reactor ends, can be an elegant solution to the problem. Indeed, the heat generated from the chemical reaction is stored in the reactor and it can be used to heat up the cold feed, thus enhancing the reaction rate. After several flow reversals, an oscillatory steady state is attained. Autothermal operations are achieved by carefully calibrating the cycle duration and feed temperature, which can be kept much lower than in conventional packed beds [1]. To date, the main industrial applications of reverse flow reactors are the catalytic oxidation of sulfur dioxide and the combustion of volatile organic compounds (VOCs) [2]. In the present work, a comprehensive model for a reverse flow reactor was developed and implemented. Axial dispersion effects were considered for both the mass and the energy balances to simulate non-ideality for the fluid phase. The chemical reaction was assumed to occur in the solid phase and, therefore, intraparticle diffusion of the reactants in the catalyst was taken into account. The influence of the cycle duration, feed temperature as well as the main kinetic and heat/mass transfer parameters was checked via a parametric investigation.
Experimental/methodology. A system of Partial Differential Equations (PDEs) appeared in the definition of the problem, which was numerically solved by the method of lines. The method replaces the spatial derivatives with a central difference approximation. To simulate the alternance of the feed and outlet positions, dedicated oscillating functions were employed.
Results and discussion. A reference simulation is displayed in Figure 1.

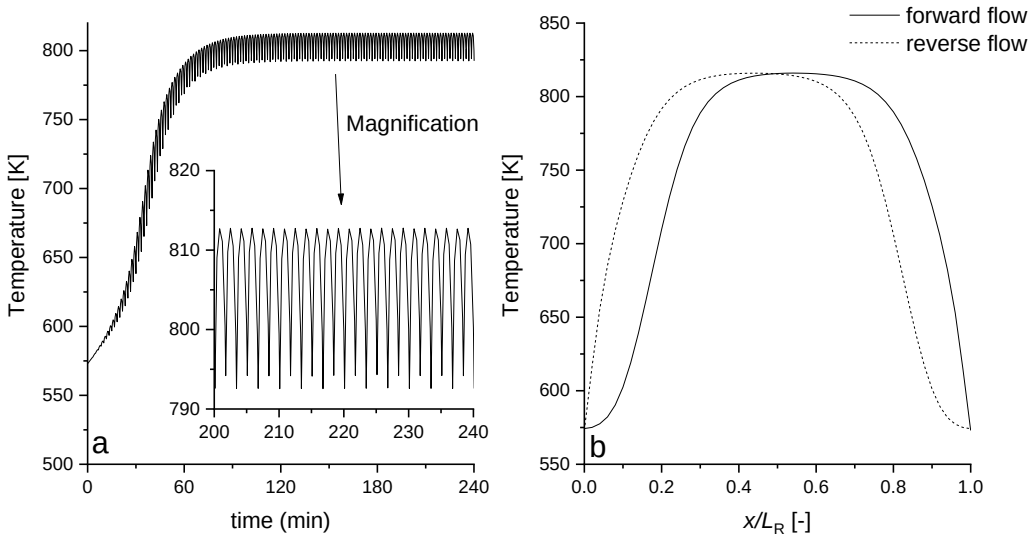

Figure 1. a) Temperature profile vs time at the reactor center. b) Temperature profile vs the dimensionless axial coordinate.

As revealed, an oscillatory steady state is attained (Fig. 1a) and a quasi-isothermal temperature profile appeared in the catalytic bed, thus improving the thermal efficiency of the catalytic process. The heat wave goes forth and back in the catalytic bed, producing two symmetric states (Fig.1b). In general, the model was very flexible even predicting even harsh operating conditions.

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Exploring the Benefits of Sorption Enhanced Reforming for Sustainable Hydrogen Production from Biorefinery Side Streams

A. Mostafa[1], I. Rapone[2], A. Bosetti[2], M. C. Romano[1], A. Beretta[1] and G. Groppi[1*]

[1] *Dipartimento di Energia, Politecnico di Milano.*
[2] *TECH/DE-R&D - Renewable Energy, Magnetic Fusion and Material Science Research Center, Eni SpA.*
[*] *gianpiero.groppi@polimi.it*

Keywords: Mathematical modelling, CO_2 capture, Sustainable hydrogen, Adiabatic reactor.

Introduction. Aiming to reach carbon neutrality by 2050, urgent measures to mitigate CO_2 emissions are needed. The supply of sustainable hydrogen streams is a key issue, increasing the interest in using waste streams and the by-products of the biorefinery as a source of low-C hydrogen [1]. However, such side streams could contain significant amounts of hydrogen; for thermodynamic reasons, this has a severe impact on the reforming process by limiting the fuel conversion. Sorption Enhanced Reforming (SER) is a promising option for achieving high yields of almost pure hydrogen from such complex streams as the continuous CO_2 removal shifts the equilibrium of the hydrocarbons steam reforming (SR) and the water gas shift (WGS) reactions towards the production of H_2. In this work, we address the effect of the H_2 content in feed of an adiabatic SER reactor using a 1D dynamic heterogeneous reactor model.

Methodology. A model of an adiabatic fixed bed reactor was developed on the gProms® platform consisting of mass and energy balances of two well mixed solid phases (sorbent and catalyst) and of the gas flow phase. Ni based reforming catalyst and CaO as a regenerable CO_2 sorbent are assumed for this study, and the kinetics of the process are obtained from literature. The modelling of the individual phases highlights the role of each on the thermal behavior of the bed and the global performance of the reactor.

Results and discussion. SER combines SR, WGS, and CO_2 sorption reactions in a single reactor. The latter is a gas solid reaction that proceeds until saturation of active sorbent, making the process dynamic in the fixed bed configuration. The overall performance of the process was evaluated based on key performance indices (KPIs) calculated as integrals from the start of feeding to the breakthrough time at varying inlet H_2 feed content. As shown in Figure 1, presenting the effect of the H_2 content in the feed on the KPIs, the increased content of hydrogen in the feed hinders the integral CH_4 conversion, reducing the net H_2 productivity and the efficiency of CO_2 capturing. For a CH_4 stream fed to the SER reactor working at an initial solid temperature of 700°C and inlet gas temperature of 600°C, a pressure of 10 bar, with space velocity of 365 $Nm^3/m^3_{rec}h$ (3646 $Nm^3/m^3_{cat}h$), the CH_4 conversion dropped from 90% to 82% passing from a feed of pure CH_4 to a stream containing 40% mol H_2, and the carbon capture ratio (CCR) decreased from 86% to 80%. Nevertheless, to achieve the same result (82% conversion and high purity produced H_2 from a 40% H_2-diluted stream), a conventional externally heated steam reforming should be run at about 765°C and combined with downstream WGS reactors, H_2 purification and CO_2 capturing unit.

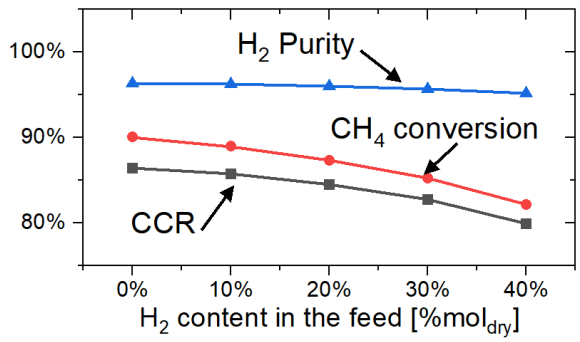

Figure 1. Effect of H_2 presence in the feed on the KPIs of the SER process.

Extending the analysis to include C2+ hydrocarbons, higher fuel conversion and CCR values are found with a conversion of 88% and CCR of 83% calculated for a stream of 10% C_3H_8, 50% CH_4, 40% H_2 fed to the SER reactor at the same working conditions. This conversion value could be achieved running a conventional externally heated steam reforming at about 780°C to fully convert the higher hydrocarbons and limit the extensive methanation.

Acknowledgments

A. Mostafa would like to gratefully acknowledge ENI S.P.A for the Phd scholarship.

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CO_2 methanation: Effect of H_2 load fluctuation on the performance of a monolithic reactor.

Douglas E. Pérez Vilela[1], Ximena García C.[2*]

[1] *Department of Chemical Engineering, University of Concepcion, Faculty of Engineering (Chile)*
[*] *xgarcia@udec.cl*

Introduction. The monolithic honeycomb reactor has proven to be an attractive technological proposal to be used in CO2 methanation since it presents a lower resistance to mass/heat transport and a negligible pressure drop in contrast to the fixed-bed adiabatic reactor [1]. On the other hand, the reactor must respond quickly and adequately to the disturbance of the H_2 load, being this type of reactor an excellent option for this [1]. As a contribution, the effect of the fluctuation of the H_2 load on the performance of this equipment in CO_2 methanation was studied, using an axial symmetric, heterogeneous, and non-stationary 2D mathematical model on a full scale.

Methodology. First, a base case was considered, where $NiAl(O)_X$ was selected as the catalyst with the kinetics of Koschany et al., 2016. A step-type reduction of 20 % of the H_2 load was chosen. The effect of the type of catalyst and the consideration of the Reverse Water Gas Shift (RWGS) on the performance of the monolithic reactor before the perturbation of the H_2 load were also studied. A 0.5 wt. % Ru/γ-Al_2O_3 catalyst with the kinetics of Falbo et al., 2018 (Case 1) and a 5 wt. % $Ni_{0.4}Co_{0.6}/SiO_2$ catalyst prepared by our research group [2] (Case 2) were used, where the RWGS is considered as an additional reaction for this.

Results and discussion. In Figure 1.a. the recovery time to the new steady state ($t_{rec,EE}$) is shorter for case 1 compared to the base case and case 2. Additionally, the maximum temperature of the reactor (T_{max}) is lower and remains practically constant throughout the dynamic operation of the equipment, especially for case 2. It can also be seen that the location of the hot spot in the dimensionless axial coordinate (z/L) is farther from the reactor inlet for case 1 (in case 2 no hotspot was observed (z/L = 1) during dynamic operation of the reactor). These trends are consistent with what has been mentioned for Ru in the literature (higher dynamic/thermal stability compared to Ni [1]). In Figure 1. b, the highest CO_2 (XCO_2) conversion at the reactor outlet (z/L = 1) is obtained for the base case, because of a higher reaction rate than other cases. For case 2, the trends observed above are generated by the combination of Ni with Co and the use of other support. It is also important to mention that the yield towards methane was 21 % for case 2, implying that the RWGS prevailed for the operating conditions proposed in this study. This has the effect of reducing the temperature increase caused by the heat of reaction released in the methanation of CO_2, thus observing an additional effect that helps improve thermal/dynamic stability compared to other cases. In conclusion, there is an important effect of the fluctuation of the H_2 load on CO_2 methanation performance when changing the catalyst and considering the RWGS reaction. These factors are important to improve the stability of the dynamic operation of this reactor in an industrial application.

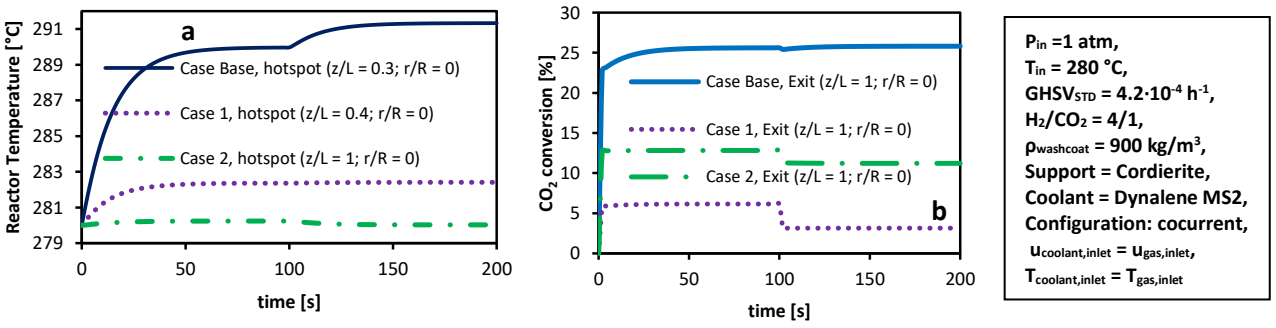

Figure 1. Temperature (a) and conversion (b) profile in the centerline of the reactor (r/R = 0) as a function of time. The dimensions and physical properties of the reactor of ref. [3]

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Metal-loaded highly porous BINAP containing polymers for the decomposition of formic acid to H_2 and CO_2

S. Seidel[1*], P. J.C. Hausoul[1], R. Palkovits[1]
[1]*RWTH Aachen University, Chair for Heterogeneous Catalysis and Technical Chemistry*
[*]*Seidel@itmc.rwth-aachen.de*

Keywords: Hydrogen, energy carrier, formic acid, catalysis, heterogeneous catalyst, solid molecular catalyst (SMC), single-site catalyst, ruthenium, covalent organic framework (COF)

Introduction.
A sustainable future of the chemical industry and our society necessitates an efficient utilization of resources. Limiting the use of precious metals such as ruthenium, palladium or platinum during chemical reactions and adopting novel carbon feed streams such as CO_2 over fossil fuel based resources are key factors to achieve this. One promising strategy for the storage of hydrogen generated by water electrolysis unifying these two concepts is the utilization of solid molecular catalysts (SMCs) for the decomposition of formic acid (FA) to and synthesis of formic acid from CO_2 and H_2. SMCs offer a fusion of the high activity of homogeneous catalysts and the straightforward handling and recycling of heterogeneous catalysts.[1, 2]

Experimental.
Based on a procedure previously reported by Wang et al., a new versatile subclass of BINAP containing SMCs for the formic acid decomposition reaction was developed utilizing a Pd catalyzed Suzuki crosscoupling polymerization reaction of brominated BINAP oxide and a aromatic boronic ester (Fig. 1).[3, 4]

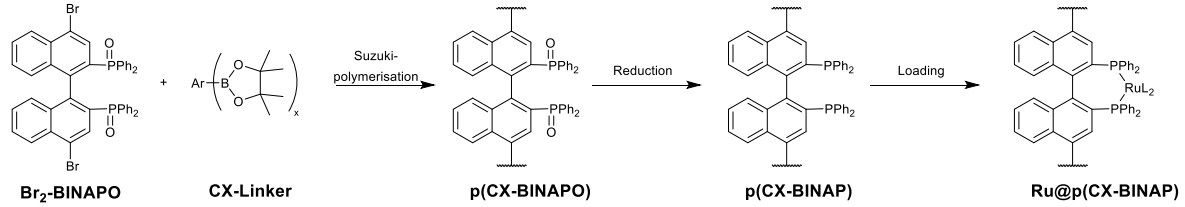

Fig. 1 Synthesis of RuL_2@p(CX-BINAP) catalysts via $Pd(PPh_3)_4$ catalysed Suzuki cross-coupling reaction, reduction via transfer oxygenation with PPh_3 and $HSiCl_3$ and loading via wet impregnation in MeOH.
After the phosphine oxide moieties in the polymeric material were reduced by a transfer oxygenation utilizing PPh_3 and $HSiCl_3$ and wet impregnation of the obtained supporting material using noble metal salts, the catalytically active materials were obtained. Subsequently, the SMCs were investigated for their activity in the decomposition of aqueous formic acid to H_2 and CO_2 in batch and continuous reactions.

Results and discussion.
A series of SMCs containing BINAP moieties with tuneable surface areas exhibiting turnover frequencies (TOFs) of up to 134 000 h^{-1}, turnover numbers (TONs) of up to 921 000 and selectivities of up to 99.97 % in the decomposition of formic acid were obtained after wet impregnation with different ruthenium salts. We propose the active catalyst species in pristine samples to be Ru single sites as confirmed by HR-TEM and XPS measurements of pristine catalyst samples.

Acknowledgments
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Impact of synthesis parameters on the activity of Cu/ZnO/ZrO_2 catalysts prepared by flame spray pyrolysis for CO_2-methanol synthesis

M. L. Schulte[1,2], V. C. Sender[1,2], L. Baumgarten[1,2], E. Saraçi[1,2]*, J.-D. Grunwaldt[1,2]*

[1]*Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany;* [2]*Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*

*Corresponding authors**:** *grunwaldt@kit.edu; erisa.saraci@kit.edu*

Introduction:

One approach to mitigate CO_2 emissions is the Power-to-Liquid (PtL) concept which converts green H_2 and CO_2 to liquid fuels/chemicals, such as methanol.[1] The hydrogenation of CO_2 to methanol, compared to conventional methanol synthesis from syngas (CO and H_2), is thermodynamically unfavored and the higher water content in the product stream leads to faster catalyst deactivation.[2] The modification of the widely applied methanol catalyst Cu/ZnO/Al_2O_3[1] with ZrO_2, instead of Al_2O_3 prompts a higher tolerance against water-induced deactivation.[3] Flame spray pyrolysis (FSP) is a fast and reproducible catalyst synthesis method which allows tuning of particle size, crystallinity and morphology by varying parameters, *i.e.* precursor feed rate, solvent, concentration, etc.[4] We used FSP to generate Cu/ZnO/ZrO_2 catalysts with different particle sizes to study their influence on activity in CO_2-methanol synthesis.

Experimental/methodology:

By varying the feed rate (2 – 12 mL/min) of precursors (Cu acetate monohydrate, Zn acetate dihydrate, Zr oxide 2- ethylhexanoate dissolved in MeOH/EHA 1:1) a series of Cu/ZnO/ZrO_2 catalysts was synthesized *via* FSP. The catalysts were thouroughly characterized by XRD, ICP-OES, BET, STEM-EDX and H_2-TPR. Prior to the reaction the catalysts were reduced in 10% H_2 in N_2 at 275 °C. CO_2 methanol synthesis conditions (3:1 H_2:CO_2 in N_2) were applied at 235 °C and different pressure ranging from 1-40 bar.

Results and discussion:

Applying a lower feed rate leads to a smaller flame. Hence, the particles have a shorter residence time in the flame preventing larger particle formation and crystallization.[5] X-ray diffraction patterns show an increase in crystallinity and crystallite size with increasing feed rate, as previously reported for other systems[6], which could also be confirmed with STEM-EDX. The catalytic performance in CO_2-methanol synthesis is shown in Figure 1 for three catalysts. The catalyst synthesized with 2 mL/min feed rate shows the highest selectivity towards methanol but the lowest CO_2 conversion. The opposite trend was observed for the catalysts prepared at 5 and 8 mL/min which show higher activity accompanied with a loss in selectivity. Since the particles become larger with a higher feed rate, this may indicate that the reaction is structure-sensitive and dependent on the particle size. Our work acts as basis to obtain a more fundamental understanding of this attractive catalyst system.

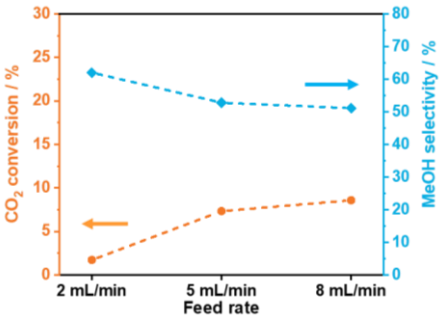

Figure 1: CO_2 conversion (orange) and methanol selectivity (blue) of catalysts prepared with different feed rates (reaction conditions: 20 bar, 235 °C, 85% H_2:CO_2 = 3:1 in N_2, WHSV = 36 L/g_{cat}·h).

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Advanced catalyst design for the H_2-efficient synthesis of dimethoxymethane from methanol

N. Simitsis[1], C. Mebrahtu[1], R. Palkovits[1*]

[1]*RWTH Aachen University, Institute of Technical and Macromolecular Chemistry, Aachen, Germany*
[*]*Palkovits@itmc.rwth-aachen.de*

Keywords: Dimethoxymethane, H2-efficient, Hβ zeolite, structure-activity relationship

Introduction. Dimethoxymethane (DMM), the shortest of the homologous oxymethylene ethers (OME_x) with the general structure $H_3C\text{-}O\text{-}(CH_2O)_x\text{-}CH_3$, is a promising diesel additive since it has the potential to decrease harmful soot emissions during combustion, thus eliminating the typical soot NO_x tradeoff. Besides, intensive research is being made to sustainably produce DMM from CO_2 and renewable H_2 feedstocks. Yet, its current production relies on an oxidative pathway where the stoichiometrically produced H_2 is directly oxidized and H_2O is formed as by-product. Our group thus recently presented a novel DMM synthesis strategy *via* the gas-phase nonoxidative dehydrogenation of methanol, where H_2 is produced as by-product instead of H_2O.[1-4] The potentially closed H_2 circulation significantly improves the overall energy efficiency of the process, making this approach highly attractive.

Experimental/methodology. For selective DMM synthesis *via* dehydrogenation of methanol, a bifunctional catalyst with both acidic and dehydrogenative sites is required. Our group previously designed a Cu/Hβ-zeolite catalyst, where a high SiO_2/Al_2O_3 ratio (520) is achieved by dealumination of the zeolite, and on which afterwards 1 wt.% Cu is loaded by incipient wetness impregnation.[1] Combining these results with literature research,[5] Ag was introduced as dehydrogenative metal instead of Cu on the optimized Hβ support. Ag/Hβ was then tested as catalyst in the non-oxidative dehydrogenation of methanol to DMM in a fixed-bed continuous flow gas-phase reactor setup and parameters such as Ag loading, catalyst pre-treatment, and reaction temperature were optimized. Furthermore, stability tests and various characterization techniques, *e.g.*, XRD, ICP-OES, H_2-TPR, FTIR spectroscopy, and N_2-physisorption, were performed, to shed light on possible structure-activity relationships.

Results and discussion. The current Cu/Hβ catalyst shows high DMM selectivity (81.5%) with a methanol conversion of 3.7% after 1500 min time on stream (TOS) at 200 °C.[1] However, a long induction time of 800 min, low stability, and low conversion when compared to the calculated equilibrium conversion (7.6%) are the existing challenges upon using the Cu/Hβ catalyst. When using the optimized Ag/Hβ, improved catalyst stability as well as a shorter induction time (600 min) could be achieved, while maintaining high DMM selectivity (73.1%) with a methanol conversion of 2.1% after 1500 min at 240 °C.[2] Interestingly, no formaldehyde is formed when increasing the reaction temperature to 280 °C when using Ag/Hβ as a catalyst, suggesting a well kinetic matching between the dehydrogenative and acidic functionalities of Ag/Hβ. H_2-TPR and XRD results show that both Ag_2O and metallic Ag^0 species are present on the catalyst. These results leave room for deeper investigations on possible structure-activity relationships, such as PDF and *in situ* FTIR analysis.

Acknowledgments
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Confined Impinging Jet MicroReactor for continuous high-throughput synthesis of nanoscaled electrocatalysts including CFD modeling

Tanja Modl[1], Aline Clausing[1], Nicholas Lynn[1], Sabine Schmitz-Stöwe[1], Thomas Schwarz[1], Klaus Stöwe[1]

[1]*Chemnitz University of Technology, 09111 Chemnitz, Germany*
[*]*klaus.stoewe@chemie.tu-chemnitz.de*

Keywords: micromixer synthesis, MicroJet Reactor (MJR), Confined Impinging-Jet MicroReactor (CIJMR), continuous-flow synthesis, mixed metal oxides, precious metall nanoparticles, platinum nanoparticles, platinum nickel nanoparticles, core/shell nanoparticles, fuel cell catalysts

Introduction. In this contribution we report on an actual development in the field of fabrication and new application of micro-structured devices in chemistry enabling (multiphase) mixing, reactions and heat transfer which are otherwise not possible with standard devices. In the field of material syntheses micro-structured devices allow a strict control over process parameters offering the possibility to design materials with tunable properties such as particle size distribution, shape, composition and surface properties. In turn, the mentioned features contribute remarkably to the performance of catalytic materials [1].

Experimental/methodology. We implemented a new design of a CIJMR in form of a cross mixing device analogous to the Synthesechemie (Dr. Penth) or Ehrfeld MicroJet Mixer (MJM) described by Dittert *et al*. [2]. The newly constructed MJR is completely dead volume free and allows the continuous preparation of nano-scale metal and metal chalcogenide particles by precipitation reactions from appropriate precursor solutions. Due to the short mixing times in the µs to ms range crystallite nucleation and crystal growth are well separated from another and enable concentration limited particle growth and thus nano-particle (NP) syntheses. To generate a deeper understanding of the processes within the MJR modelling was performed by the CFD program ANSYS Fluent including also chemical reactions. Our CFD modeling investigations were based on RANS, LES and DES approaches. It can also be broadened to syntheses in supercritical media as well as high-throughput approaches generating gradient libraries for high-throughput parameter screening.

Results and discussion. We started our research on the MJM with the syntheses of alternative support materials for fuel cell application to replace the standard carbon instable at typical operating conditions of PEMFC. Additionally, we applied this reactor concept by preparation of nano-scale sulfides, selenides and tellurides for photovoltaic and other applications. We widened our expertise on precious metal NP in form of single element, mixed metal (alloys/intermetallic phases) or core-shell NP by investigating the system Pt – Ni. As intended, the particle syntheses in the size range between 5 - 10 nm was successful. We also extended the reactor system and currently use a second microreactor in series of the first reactor for the syntheses of either Ni@Pt or PtNi@Pt - NP. These particles are in the focus for applications as fuel cell electrocatalysts. The stabilization of these particles was mostly achieved by chemical agents utilizing alkali metal hydroxides (Co4Cat process) [3].

All in all, we will present a significant contribution for the development of new approaches for a more effective synthesis and screening of new functional materials for industrially relevant applications.

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A cheap & staightforward synthesis of Sr promoted Ni/ZrO_2+Al_2O_3 catalyst for high performance Dry reforming of methane

A. S. Al-Fatesh[1*], A.A. Ibrahim[1], Rawesh Kumar[2], Chun-Yang Yin[3], Salma A. Al-Zahrani[4] , Ahmed E. Abasaeed[1],A.H. Fakeeha[1]

[1]*Chemical Engineering Department, College of Engineering, King Saud University, Riyadh, KSA*

[2]*Department of Chemistry, Indus University, Ahmedabad, Gujarat 382115, India*

[3]*Newcastle University in Singapore, Ngee Ann Polytechnic, Singapore*

[4]*Chemistry Department, Faculty of Science, University of Ha'il, KSA*

**Correspondence:* aalfatesh@ksu.edu.sa

Keywords: Dry reforming of methane, Ni/ZrO_2+Al_2O_3, Sr promoter

Introduction. Chemical conversion of global warming gases of CH_4 and CO_2 via dry reforming of methane (DRM) is an urgent need of this era. DRM is an endothermic reaction that cheap Ni-based catalytic active metal has opted for. A combination of ZrO_2 and Al_2O_3 support was used due to their better dispersion and thermal stability [1, 2] . The DRM reaction is: $CH_4 + CO_2 = 2H_2 + 2CO \quad \Delta H^0_{298\,K} = +247.31 \frac{kJ}{mol}$

The strontium (Sr) addition to Ni-based catalysts increases the dispersion of Ni and improves the resistance to carbon deposition [3]. The use of Sr promoter over novel ZrO_2+Al_2O_3 supported Ni catalyst can be expected to be highly efficient towards DRM. Herein, we have synthesized 5Ni+3Sr/ ZrO_2+Al_2O_3 catalyst and characterized and employed it for DRM.

Experimental/methodology. The catalyst is prepared by impregnation of the required amounts of Ni $(NO_3)_2.6H_2O$ by 5.0 wt.% loading of Ni, Sr $(NO_3)_2$ promoter over 10wt%Zr_2O_3+90wt%Al_2O_3 support. The dried, calcined and powdered catalyst is packed in a fixed bed. The catalyst is pretreated under H_2 stream at 700°C for 60 min and then switched to gas feed (3:3:1 for CH_4, CO_2, and N_2 gases) at 800°C with a space velocity of 42,000 ml/gcat h^{-1}. The outlet gas from the reactor is analyzed by GC. CH_4 and CO_2 conversions were calculated:

$$CH_4 \text{ Conversion } (\%) = \frac{CH_{4,in} - CH_{4,out}}{CH_{4,in}} \times 100 \,;\; CO_2 \text{ Conversion } (\%) = \frac{CO_{2,in} - CO_{2,out}}{CO_{2,in}} \times 100$$

Results and discussion. XRD result shows the presence of cubic ZrO_2 phase. All the catalysts have type IV isotherm. DRM reaction generated 78% CH_4 and 82% CO_2 conversions up to 430-minute time on stream at 800°C. The incorporation of Sr enhanced the basicity and moderates the NiO interaction with support. The weight loss over 5Ni+3Sr/ ZrO_2+Al_2O_3 catalyst is also minimal. All total, 3wt% Sr incorporation into 5wt%Ni/ZrO_2+Al_2O_3 catalyst brings as high as 90% CH_4 conversion and CO_2 conversion.

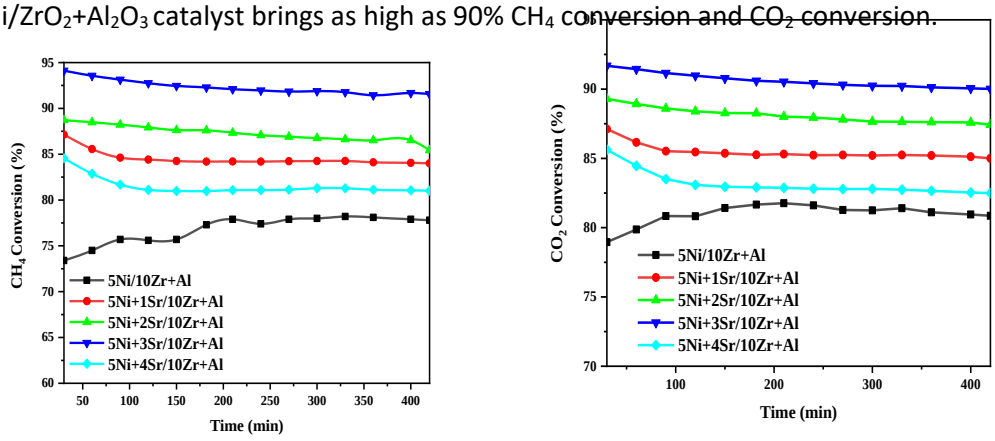

Figure CH_4 and CO_2 convesions vs Time on stream

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Electrocatalysis, including fuel cells

Strategies to improve CO tolerance and corrosion resistance of Pt electrocatalysts for polymer electrolyte membrane fuel cells

I. Borbáth[1*], K. Salmanzade[1], E. Tálas[1], Z. Pászti[1], A. Kuncser[2], Ș. Neațu[2], M. Florea[2], I.E. Sajó[3], D. Olasz[4], Gy. Sáfrán[4], A. Tompos[1]

[1]*Research Centre for Natural Sciences, Eötvös Loránd Research Network (ELKH), Budapest, Hungary*
[2]*National Institute of Materials Physics, Magurele, Romania*
[3]*University of Pécs, Szentágothai Research Centre, Pécs, Hungary*
[4]*Centre of Energy Research, Eötvös Loránd Research Network (ELKH), Budapest, Hungary*
[*]*borbath.irina@ttk.hu*

Introduction. In order to facilitate widespread use of polymer electrolyte membrane fuel cells (PEMFCs), development of more affordable systems is needed, which involves replacement of the traditional Pt/C electrocatalysts with more corrosion resistant and cheaper ones. In our previous studies this concept was realized by synthesizing anode Pt electrocatalysts with different Pt content supported on a conductive and corrosion resistant composite consisting of oxophilic metal M (M: W, Mo)-doped TiO_2 and various carbonaceous materials [1-2]. In such a unique material system, the corrosion resistance and nanoparticle-stabilizing ability of TiO_2, the good co-catalytic properties of doping metals as well as the large surface area and high conductivity of active carbon are brought together. The transition metal dopant facilitates the oxidation of CO at much lower potentials than on pure Pt, which is important when hydrogen from steam reforming is considered as fuel. Moreover, the Sn dopant is believed to promote the oxygen reduction reaction (ORR), thus Sn-doped TiO_2-carbon composites can also be used at the cathode side. The aim of the present work is the study of $Ti_{(1-x)}Sn_xO_2$-C (x: 0.1-0.3) composite supported Pt electrocatalysts.
Experimental/methodology. The synthesis of novel $Ti_{(1-x)}Sn_xO_2$-C (x: 0.1-0.3, C: Black Pearls 2000 (BP), CABOT)) composite supports with mass ratio of the $Ti_{(1-x)}Sn_xO_2$/C= 75:25 and 25/75 was performed by multistep sol-gel synthesis followed by high-temperature treatment (HTT) in Ar. Raman spectroscopy, XRD, XPS, SEM/EDX and TEM were used to characterize the bulk and surface microstructure. Electrocatalytic performance of the 20 wt.% Pt catalysts was studied by cyclic and CO_{ads}-stripping voltammetry measurements combined with long-term stability test; catalytic activity of the catalyst samples was also tested in the ORR and hydrogen oxidation reaction (HOR) by rotating disc electrode technique [2].
Results and discussion. The electrocatalysts prepared according to an adapted method developed for Mo-containing composites [2] consisted of rutile crystallites and metallic Sn in a small amount (1-2%), had an inhomogeneous microstructure and exhibited unusually low electrochemical surface area (ECSA) (~30 m^2/g_{Pt}). To avoid these shortcomings, the synthesis of the Sn-containing composite was modified by simultaneous introduction of the precursors of Sn and Ti at the beginning of the synthesis, before the addition of carbon and the aging step. We demonstrated that the composites and Pt electrocatalysts obtained using this preparation route were free of segregated Sn^0 or SnO_2 phases, possessed a more homogeneous/uniform mixed oxide distribution, and the ECSA values were comparable to those obtained on Mo-based composites of similar composition (~60-80 m^2/g_{Pt}). In order to clarify the possibility of using these catalysts as anode or cathode in PEMFCs, their electrocatalytic characteristics were investigated in the ORR and the HOR. A sharper increase in the HOR current observed on Sn-containing catalysts compared to Pt/C indicated the efficiency of this catalytic system. It has been demonstrated that the behavior of electrocatalysts mainly depended on the synthesis route used in the preparation of the composite support materials and was not influenced by the Ti/Sn ratio.

Acknowledgments
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Well-defined nanocatalysts for selective CO_2 electroreduction

R. Buonsanti[1*]

[1] *Laboratory of Nanochemistry for Energy (LNCE), Institute of Chemical Sciences and Engineering (ISIC), École Polytechnique Fédérale de Lausanne, CH-1950 Sion, Switzerland*
[*] *raffaella.buonsanti@epfl.ch*

The electrochemical CO_2 reduction reaction (CO_2RR) offers the opportunity to convert CO2 into fuels and chemical feedstocks, while mitigating anthropogenic CO2 emissions and storing renewable energy. Multi-carbon (C_{2+}) compounds (e.g., ethylene, ethanol, propanol) are among the most attractive CO_2RR products owing to their commercial value and high energy densities. However, optimizing the selectivity of CO_2RR electrocatalysts towards one particular product remains a crucial challenge that is not trivial to .address because multiple intermediates are involved in the CO_2 to C_{2+} conversion pathway
In these context, unambiguous relationships between the activity, selectivity and stability of the catalyst .with its structure and composition becomes crucial to make concrete progress in this field
In this talk, I will showcase a few examples which highlight how shape-controlled nanocrystals can contribute to address the selectivity challenge in CO_2RR. First of all, I will discuss how size control of Cu nanocubes and Cu octahedra has revealed the importance of facet-ratio to maximize the selectivity towards ethylene and methane, respectively. Second, I will present our recent computational-experimental efforts towards using well-defined NCs, in the framework of a tandem scheme based on the coupling of Cu nanocrystals with CO-generating Ag, to elucidate selectivity rules at the hydrocarbons/alcohols branching nodes in the CO_2RR pathway and increase ethanol production. Finally, I will discuss a few examples .adressing catalyst stability during CO2RR, a topic which is still underexplored

Toward Enhancement of Activity of Low-Pt-Content-Electrocatalysts for Oxygen Reduction

Pawel J. Kulesza*, Iwona A. Rutkowska, Aldona Kostuch, Sylwia Zoladek

Faculty of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland
*pkulesza@chem.uw.edu.pl

The proton-exchange membrane fuel cell (PEMFC) technology is one of the most promising approaches for energy conversion in automotive applications. The progress in this subject is greatly hindered by the high cost and scarcity of the state-of-the-art platinum-based materials which are regarded as the most effective cathode catalysts. Therefore, most of the current research studies have been devoted to the optimization of active centers and maximization of their utilization, which should allow the lowering of the cathode Pt loadings without loss of performance and durability. Unfortunately, the problem of electrochemical stability and the danger of generation of higher quantities of the undesirable hydrogen peroxide intermediate may become even more serious in the case of systems utilizing lower amounts of the Pt catalyst.

Among important strategies is the hybridization, activation, and stabilization of carbon-supported Pt catalysts by functionalization through admixing with certain nanostructured and typically substoichiometric metal oxides. Special attention is paid to application of the bi- or multi-metallic Pt-based alloys in their various forms and structures. Among other important issues are such features as porosity, hydrophilicity, and degree of graphitization of carbon components, in addition to the existence of metal–support interactions, high electrochemical active surface area, electronic structure of interfacial Pt, and the feasibility of adsorptive or activating interactions with oxygen molecules. Hybrid supports, which utilize metal oxides (e.g., CeO_2, WO_3, or ZrO_2) have been demonstrated to stabilize Pt and carbon nanostructures and diminish their corrosion while exhibiting high activity toward the four-electron (most efficient) reduction of oxygen.

The rotating ring-disk electrode (RRDE) methodology, are typically applied to diagnose mechanisms and dynamics of ORR. A tempting alternative for recording the electrochemical responses is to integrate the current and to report charge passed as a function of time. Chronocoulometry offers important advantages including good signal-to-noise ratio because the act of integration smooths random noise on the current transients. Furthermore, by integrating the responses, it is possible to separate surface phenomena (e.g. interfacial oxidation of carbon or platinum) more readily from bulk electrochemical responses (ORR).

Tailoring of Fe single-atoms on hollow carbon spheres for the oxygen reduction reaction

Rui S. Ribeiro[1,2], Ana Luísa S. Vieira[1,2], Juan J. Delgado[3,4], Rafael G. Morais[1,2], Natalia Rey-Raap[5], Raquel P. Rocha[1,2], M. Fernando R. Pereira[1,2]

[1] *LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.*

[2] *ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.*

[3] *IMEYMAT: Institute of Research on Electron Microscopy and Materials, University of Cádiz, E11510 Puerto Real, Cádiz, Spain.*

[4] *Departamento de Ciencia de Materiales, Ingeniería Metalúrgica y Química Inorgánica, University of Cádiz, E11510 Puerto Real, Cádiz, Spain.*

[5] *Instituto de Ciencia y Tecnología del Carbono, INCAR-CSIC, Francisco Pintado Fe 26, 33011 Oviedo, Spain*

Keywords: oxygen reduction, Fe electrocatalysts, single-atom catalyst, hollow carbon spheres

Introduction. Single-atom catalysts (SACs) have emerged as one of the most promising alternatives to noble metal-based catalysts for highly efficient oxygen reduction reaction (ORR)[1]. A broad range of non-platinum group metal electrocatalysts has been developed, among which Fe−N−C nanostructures have been considered one of the most promising candidates. Most strategies for the synthesis of SACs need delicate procedures. Therefore, developing strategies to tailor atomically better dispersed Fe sites in N-doped carbon supports is highly desirable. Herein, we reported the design of hollow carbon spheres with highly stable Fe centres and enhanced catalytic activity in ORR.

Experimental/methodology. Carbon spheres (CSs) were synthesized by sol-gel polycondensation through Stöber's method, followed by thermal annealing and silica etching, according to a previously reported procedure [2]. The hollow CSs were then doped with nitrogen and Fe by adapting a procedure reported elsewhere [3]. The effect of metal loading was studied by varying the proportion of metal precursor during the synthesis. In addition, the role of each precursor during the synthesis of the optimized electrocatalyst was elucidated by preparing additional materials in the absence of specific precursors. All samples were physicochemically characterized using suitable techniques, including high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy-high angle annular dark field imaging (STEM-HAADF) in combination with energy-dispersive X-ray spectroscopy (EDX). The catalytic performance of the samples in ORR was assessed by electrochemical measurements using a three-electrode cell configuration in alkaline media.

Results and discussion. The performance of the Fe-N-doped hollow CSs in ORR seems to be governed by the quality of Fe species rather than the overall Fe load. Nitrogen seems to modulate the charge density nearby the active sites and limit the agglomeration of the metal precursor during the synthesis. Glucose enhances the metal-heteroatom coordination and subsequent dispersion of active sites on the carbon surface. The activity of the best-performing metal-free CSs (CS_7Fe-N) in ORR is still far from that obtained with the commercial noble metal-containing Pt/C. Nevertheless, it is thus noteworthy that CS_7Fe-N revealed superior stability (97%) than Pt/C (92%) in the same conditions. Therefore, the methodology herein reported opens a window of possibility for the development of highly stable ORR electrocatalysts based on single-atom Fe-N hollow CSs.

Acknowledgments

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Electrocatalytic activity in the oxygen evolution reaction of ordered mesoporous carbon-supported cobalt oxide nanoparticles

T. Darvishzad[1], A. Ejsmont[2], K. Kadela[1], G. Grzybek[1], , G. Słowik[3], M. Lofek[1], J. Goscianska[2], A. Kotarba[1], P. Stelmachowski[1]*

[1]*Jagiellonian University, Faculty of Chemistry, Krakow, Poland*
[2]*Adam Mickiewicz University in Poznań, Faculty of Chemistry, Poznań, Poland*
[3]*Maria Curie-Sklodowska University in Lublin, Faculty of Chemistry, Lublin, Poland*
[*]*pawel.stelmachowski@uj.edu.pl*

Keywords: hydrogen production, mesoporous carbon, nanoparticles, surface modification, plasma oxidation, oxygen functional groups

Introduction. The effective use of the active phase is the main goal of optimisation of the supported catalysts. Carbon supports do not interact strongly with the metallic or metal oxide phases; thus, oxidative treatment is often used to enhance the number of anchoring sites for deposited particles. Oxidation treatments can deteriorate the textural properties or electrical conductivity of carbons, especially those exhibiting a well-developed porosity and a specific surface area. Cobalt spinel, Co_3O_4, is an active phase for multiple thermal (e.g. N_2O decomposition) and electrochemical (e.g. oxygen evolution reaction) catalytic processes, and its dispersion controls the overall effectiveness of the catalyst [1,2]. In this study, we set out to investigate whether the oxidation pretreatment of mesoporous carbon allows the depositing of a higher loading and a more dispersed cobalt active phase.

Experimental/methodology. We used graphitic ordered mesoporous carbon obtained by a hard-template method from KIT-6 silica as active phase support. To obtain different quantities and speciation of oxygen functional groups, we used a low-temperature oxygen plasma. By varying the generator power, pressure in the plasma chamber, and treatment time, we obtained a broad range of plasma oxidative capabilities. The oxidised carbons were then subjected to equilibrium adsorption of Co^{2+} ions from a pH 5 buffer solution. After filtering, the cobalt oxide phase was deposited by washing the filtrate with KOH. The main methods used to characterise the studied materials were X-ray photoelectron spectroscopy for surface oxygen content and speciation, along with transmission electron microscopy for the determination of the quality of the deposited cobalt oxide phase. Catalytic performance was evaluated in the oxygen evolution reaction in a three-electrode setup in chronoamperometric mode.

Results and discussion. We have found that the oxidative pretreatment of mesoporous carbon influences the speciation of the deposited cobalt oxide phase. Moreover, the activity of the electrocatalysts in the oxygen evolution is positively correlated with the relative content of COO-type groups and negatively correlated with the C=O-type groups on the carbon support. Additionally, the high relative content of COO-type groups on the carbon support is correlated with the presence of well-dispersed Co_3O_4 nanoparticles. The results obtained indicate that to achieve a better dispersed and more catalytically active material, it is more important to control the speciation of oxygen functional groups rather than to maximise their total concentration. The results obtained with the model systems were used to develop highly active oxygen evolution electrocatalysts with an active Co_3O_4 phase supported on mesoporous carbon.

Acknowledgments
This study was financially supported by the National Science Center, Poland, project number 2020/37/B/ST5/01876.

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In situ XAS investigation of carbon-supported single-site catalysts for water oxidation

Wenchao Wan,[1] Liqun Kang,[1] Zongkun Chen,[1] Serena DeBeer,[1] Robert Schloegl,[1] Saskia Heumann[1*]

[1]*Max Planck Institute for Chemical Energy Conversion, 45470 Mülheim an der Ruhr, Germany*

Keywords: carbon material, in situ X-ray absorption spectroscopy, single-atom catalysis, water oxidation

Introduction. Atomically dispersed single metal atoms on highly conductive carbon support have emerged as a new catalyst class for electrocatalysis. Metal species in the form of single-site catalysts (SSC) well coordinated with non-metal atoms on the carbon support, such as N and C, which contains both the features of molecular and heterogeneous catalysis, provide an ideal platform for mechanistic study.[1-3] However, study on the structural evolution of this type of catalyst to acquire the real active species has barely reported. Herein, a novel and convenient coordination strategy was reported to construct a series of SSCs containing the most widely studied transition metals (Fe, Co, Ni) in the form of a single element (Fe/Co/Ni) and dual elements CoFe and NiFe. The atomic feature of the as-prepared SSCs was systematically characterized by a series of techniques, such as high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and X-ray absorption spectroscopy (XAS). The oxygen evolution reaction (OER) performances of SSC show that two metal elements (CoFe and NiFe) are superior to these of SSC with a single metal element. In situ XAS together with the post-HAADF-STEM measurements clearly show that the newly formed new active species containing the M-O-M moieties during the OER is the real active sites.

Experimental/methodology. The catalysts were synthesized through a coordination strategy combined with a pyrolysis process. In particular, a molecular containing phenol groups was used as the ligand to coordinate Fe, Co, and Fe ions in water, and further mixed with C/N containing complex. The mixture was subjected to a pyrolysis process in an inert atmosphere to obtain the final catalysts.

Results and discussion. The atomistic dispersion of the metal elements on carbon was directly observed through HAADF-STEM as shown in **Figure 1a**. The metal content ranges around 3-5 wt.% determined by EDX. The local structure of the metal centers was identified by XAS and other spectroscopic techniques. All these results indicate the atomic dispersion of the metal species on carbon, and the metal atoms are well coordinated by the non-metal N/O atoms. In situ XAS measurements together with post-HAADF-STEM measurements demonstrate that the structural restructure occurred to all the SSCs during the OER which promotes the formation of hydroxides or oxides containing the typical M-O-M (M=Fe, Co, and Ni) moieties **Figure 1b-d**. In addition, the coordination and the oxidation of the metal centers also vary under different potentials. Our research offered strong experimental evidence in the structural reconstruction of the carbon-supported single-site catalysts for the OER, which may reflect the fact that carbon-supported SSC act as a pre-catalyst instead of the real active phase for the OER.

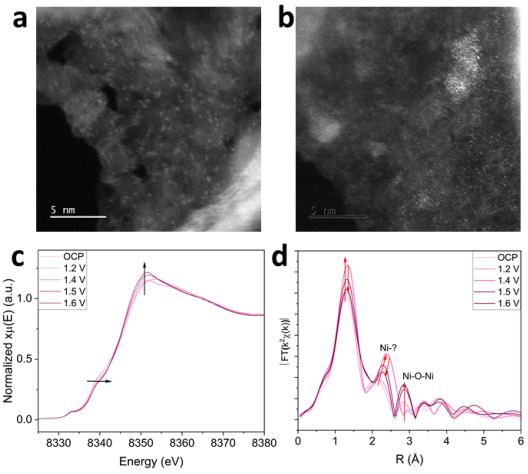

Figure 1. HAADF-STEM images of the Ni SSC (a) before and (b) after the OER. (c-d) In situ XAS spectra of Ni SSC under the OER.

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Electrocatalysts for Alkaline Oxygen Reduction and Evolution Reactions

S. Wierzbicki[1,2], T. Darvishzad[1], J. Gryboś[1], P. Stelmachowski[1], Z. Sojka[1], K. Kruczała[1*]

[1]Faculty of Chemistry, Jagiellonian University in Krakow, Gronostajowa 2, 30-387 Krakow, Poland.
[2]Doctoral School of Exact and Natural Sciences, Jagiellonian University in Krakow, Gronostajowa 2, 30-387 Krakow, Poland.
kruczala@chemia.uj.edu.pl

Introduction. The growing global demand for energy combined with the need to protect the natural environment, makes the development of an alternative to fossil fuels, clean energy sources a crucial issue. Hydrogen has been considered one of the most promising chemicals for energy storage, which can be converted back into heat and electrical energy. The most efficient way to generate electricity from hydrogen is the fuel cell (FC) technology. In the recent decade, a significant amount of research has focused on the development of anion-exchange membranes (AEMs) and oxygen reduction and evolution reaction (ORR and OER) catalysts to be used in AEMFCs [1-4].

Experimental/methodology. Multi-walled carbon nanotubes (MWCNTs) doped with nitrogen and sulfur atoms and with deposited manganese–cobalt spinel catalysts were studied to reveal the role of active centers in the ORR and OER in alkaline media. Commercial MWCNTs were oxidized by boiling in concentrated nitric acid and then doped with N and S heteroatoms using thiourea precursor. Manganese-cobalt spinels supported on the MWCNTs were synthesized by a microwave-assisted solvothermal route. The catalysts were comprehensively characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy (RS), and X-ray fluorescence spectroscopy (XRF).

Results and discussion. The spinel active phase consists of well-dispersed nanocrystals with sizes in the range of 5-8 nm. The electrocatalytic activities in ORR and OER were examined in alkaline media by rotating ring-disc electrode (RRDE) and rotating disc electrode (RDE) techniques, respectively. It was found that N- and S-doped MWCNT catalysts exhibit high activity in ORR with $E_{onset} \approx 0.890$V, and a number of electrons exchanged $n \approx 3.83$, which remained essentially the same, within experimental error, upon spinel deposition (**Figure 1a**). The addition of the spinel phase does not improve the electrocatalytic properties. The advantage of the dispersed spinel active phase was observed in OER, the activity of these samples was comparable to that of the RuO_2 benchmark catalyst (**Figure 1b**). The calculated bifunctional potential gap values, $\Delta E = 0.78$ V, confirm the high activity of the developed catalysts. In the case of ORR, the observed reactivity was accounted for by the incorporation of nitrogen and sulfur to the MWCNTs, whereas for OER the locus of the active centers is moved towards the manganese-cobalt spinel nanocrystals dispersed on the MWCNTs matrix. Functionalization of the latter with N and S atoms is then catalytically redundant.

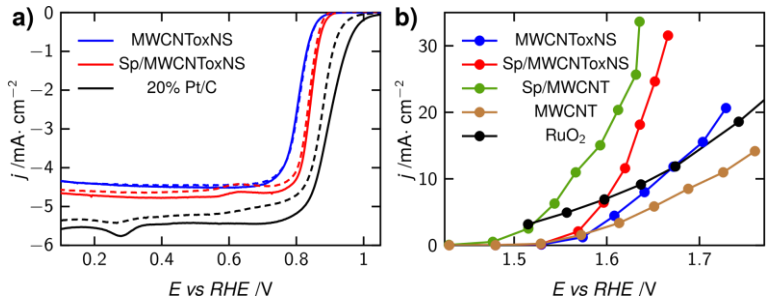

Figure 1. LSV profiles recorded during ORR (**a**), and OER I-V curves **(b)** at 1600 RPM in O_2 and Ar-flushed 0.1 M KOH solution, respectively.

Acknowledgments

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Activity and durability of hierarchical Fe-doped $Ni(OH)_2$/Ni catalysts for alkaline oxygen evolution reaction: In situ XANES studies

Sang-Yeon Lee[1], Yong-Kul Lee[1*]

[1]*Department of Chemical Engineering, Dankook University, 152 Jukjeonro, Yongin 16890, South Korea*
[*]*yolee@dankook.ac.k*

Keywords: NiFe-LDH, alkaline oxygen evolution reaction, XANES

Nature of activation and degradation of NiFe layered double hydroxide (NiFe-LDH) and hierarchical Fe-doped Ni(OH)2/Ni has been explored using in situ X-ray absorption near edge structure (XANES) spectroscopy coupled with cyclic voltammetry (CV) in a potential range of 0–0.9 V (vs. Hg/HgO). A series of NiFe-LDH samples have been prepared by electrodeposition with varying Ni/Fe molar ratios from 99:1–16:84. Fe has been doped on Ni(OH)2 and anodized Ni as Fe-Ni(OH)2 and Fe-ANi, respectively. The case of conventional NiFe-LDH, obtained by the co-electrodeposition, presents lower overpotential in OER than Ni(OH)2, but still shows 15% degradation during 100 CV cycles. The in situ XANES analysis confirmed that γ-NiOOH was still isolated during CV cycles, as seen in Ni(OH)2. In contrast, Fe-doped Ni(OH)2 obtained by adding 20 ppm of Fe to the electrolytes (Fe-Ni(OH)2) led to a lower overpotential and showed high activity and stability during 100 CV cycles. To realize a better conductivity environment, anodic oxidation of Ni was applied at 3 V to obtain Ni(OH)2 on the surface of the Ni phase (ANi). It shows even better activity and stability than NiFe-LDH. The Ni phase of Fe-ANi is maintained as Ni2+ regardless of potential changes. Fe-ANi also shows a lower white line intensity and a higher pre-edge intensity in the Fe K-edge XANES, which proves the adsorption of Fe on the surface of Ni. Overall, these findings provide important insight that a highly active and durable OER catalyst can be obtained by anodic pretreatments of Ni foam followed by Fe-dopping.

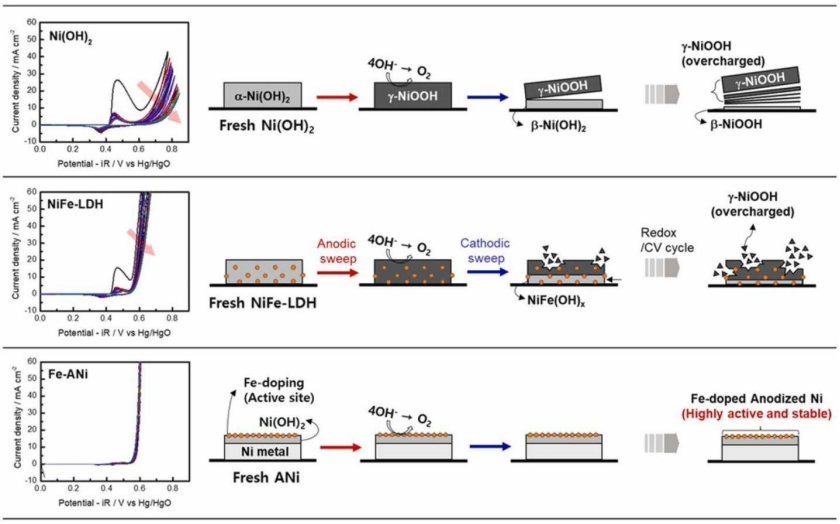

Fig. 1 Electrochemical performances of NiFe-LDH and the proposed activation and degradation mechanism in the OER

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CuCr Catalysts For Ammonia Electro-Oxidation: A Study On Activity And Selectivity

Annie Cleetus[1*], Hanan Teller[1], Alex Schechter[1]

[1] *Department of Chemical Sciences, Ariel University, Israel*

**e-mail: annieclEetus2@gmail.com*

Keywords:Ammonia oxidation, electro-catalyst, bimetallic catalyst, non-noble catalyst

Introduction.

Ammonia is considered as one of the most efficient hydrogen carrier, as it contains 17% of H_2 by weight. Being carbon free at the end use, energy generation from ammonia (NH_3) has become a matter of interest in the past years. In the efficient conversion of ammonia to electricity in fuel cell technologies, such as portable power sources, a major challenge is the identification of a suitable catalyst that can selectively oxidize NH_3 to N_2 at low over potentials, and ambient pressure and temperature, at high rates. In this work, low cost bimetallic carbon supported CuCr catalysts which were found to be more active than elemental Cu and Cr were prepared and tested for activity and selectivity towards AOR.

Experimental/methodology.

A simple sodium borohydride reduction method was used for the synthesis of the catalyst. The formation of alloy was confirmed through PXRD. AFM and HR-SEM was used for further characterization of the nano-particles. Electrochemical measurements were performed using a potentiostat to study activity and stability. Online mass spectroscopy and UV-Visible spectroscopy was used to identify the byproducts of the process.

Results and discussion.

The CuCr activity was found to increase with Cu content, however it was higher than pure Cu, which reveals a synergistic effect between Cu and Cr in the oxidation of NH_3, due to electronic interactions between Cr and Cu [1]. Cyclic voltammetry on stable catalysts with 90% Cu in 0.1 M KOH and 0.1 M NH_3 revealed a peak current density of 22 mA/mg at a scan rate of 20 mV/s compared with 0.04 mA/mg for Cr and 6.9 mA/mg for Cu under the same conditions (Fig 1.). PXRD measurements have revealed the presence of oxides and hydroxides of Cu and oxides of Cr along with the metallic phases on the electrode surface that contributes to the activity of the catalyst. Mass spectrometry measurements have identified N_2 as the major product of oxidation along with trace amounts of N_2O and N_2H_4. Subsequent LSV coupled with chronamperometry at 1.1 V (vs RHE) in 0.1 M KOH and 0.1 M NH_3 for 1hr has shown an increase in peak current density for the initial 3hrs followed by a decrease suggesting the saturation of the active sites in the first 3 hrs of oxidation. Pre-oxidation in KOH was found to improve the activity and stability of the catalyst over time. Dissolution of Cu and Cr (CrO_4^{2-}) into the solution has also been identified through ICP and UV-Vis spectroscopy. 90% Cu catalyst of CuCr in similar conditions show higher peak current density compared to commercial Pt catalyst (14.8 mA/mg) thus corroborating the potential of CuCr based catalysts for ammonia oxidation in fuel cells in the future.

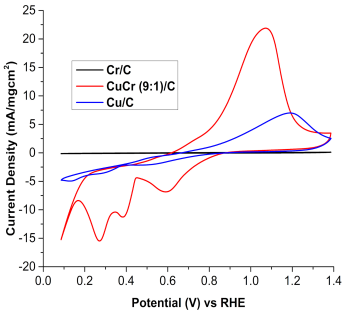

Figure 1: Variation of current density Vs potential of the catalysts in 0.1M KOH and 0.1M NH_4OH solution at a scan rate of 20mV/s.

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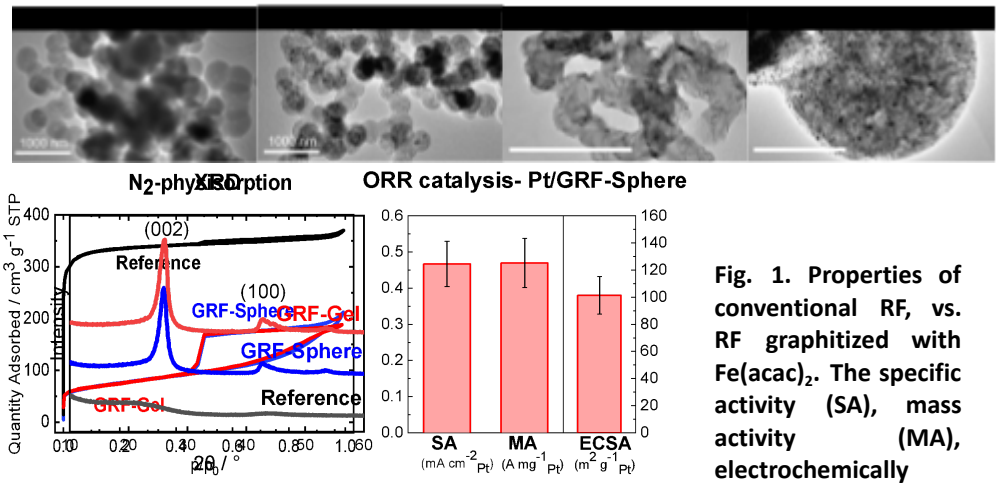
Porous graphitized Resorcinol-Formaldehyde (GRF) spheres/gels as highly stable supports for PEM fuel cells

H. Hosseini[1], A. Gunnarson[1], N. K. Tran[1], T. Imhof[2], M. Ledendecker[2,3], F. Schüth[1*]

[1] *Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany*
[2] *Technical University of Darmstadt, Darmstadt, Germany*
[3] *Technical University of Munich, Munich, Germany*
[*] *schueth@kofo.mpg.de*

Introduction. Carbon materials are desirable for electrocatalysis, owing to their superior conductivity, stability, and structural tunability. Platinum and platinum alloys supported on carbon blacks (CBs) are benchmark catalysts for Proton Exchange Membrane Fuel Cells (PEMFCs). Platinum confinement in the pore system of mesoporous carbon prepared by hard-templating was shown to suppress catalyst degradation in PEMFCs.[1] Despite the precise control over the morphology, the template removal and low yield restrict industrial application. As a remedy, we establish an easy synthesis of carbon gels through sol-gel polymerization of resorcinol (R) and formaldehyde (F), ultimately resulting in graphitic mesoporous carbons.
Experimental/methodology. The general reaction consists in mixing R and F in the presence of a basic catalyst. Then, the solution is heated for a certain time to obtain crosslinked gels.[2] By incorporation of specific metal salts, we synthesize mesoporous and highly graphitic carbon spheres (GRF-Sphere) in a simple way without employing any hydrothermal steps, solvent exchanges, supercritical drying, or post-activation techniques.
Results and discussion. The conventional carbonized RF spheres are not suitable for PEMFCs, as they are commonly non-graphitic and microporous (Fig. 1.). However, modification of the synthesis route allowed the production of mesoporous, highly graphitic carbon spheres (GRF-Sphere), thanks to the porogenic and graphitization effect of $Fe(acac)_2$. Pt nanoparticles with an average size of 3 nm were deposited in the pores of GRF-spheres by incipient wetness impregnation and subsequent annealing. The catalyst Pt/GRF was highly active for the ORR, i.e., with a specific acitivity > 0.45 mA cm^{-2}_{Pt}. The stabilization of the active phase by pore confinement was demonstrated with an accelerated stress test in the typical operating range of a PEMFC (Fig. 1). Pt/GRF retained a significantly higher share of active surface area compared to a common Pt/Vulcan catalyst. When the concentrations of R and F were increased 25-fold, a graphitic, mesoporous gel (GRF gel) was obtained at a volume yield of 70 g L^{-1}, underlining the potential of this process for industrial application.



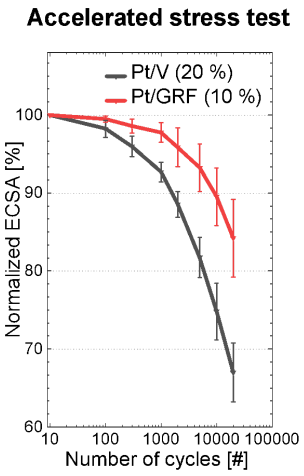


Fig. 1. Properties of conventional RF, vs. RF graphitized with $Fe(acac)_2$. The specific activity (SA), mass activity (MA), electrochemically active surface area (ECSA) of Pt/GRF and stability results in comparison to Pt/Vulcan are shown.

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The role of ligand heteroatoms in electrocatalytic hydrogen evolution by iron(II) N-heterocyclic complexes

J. S. Pap[1*], S. Keszei[2], T. Ollár[1], L. Tapasztó[2]
[1] *Surface Chemistry and Catalysis Department, Centre for Energy Research, Hungary*
[2] *Institute of Technical Physics and Materials Science, Centre for Energy Research, Hungary*
Corresponding Author's E-mail address: pap.jozsef@ek-cer.hu

Keywords: hydrogen evolving reaction, iron complex, electrocatalysis

Non-noble metal-based systems are intensely studied in the electrocatalytic hydrogen evolution reaction (HER) as cost-efficient substitutes for platinum. In this study, we report the catalytic behavior of four Fe(II) complexes containing the bidentate ligands 2-(2′-pyridyl)benzoxazole ($\mathbf{L^{O}}$), 2-(2′-pyridyl)benzthiazole ($\mathbf{L^{S}}$), 2-(2′-pyridyl)benzimidazole ($\mathbf{L^{NH}}$) and 2-2′-bipyridyl ($\mathbf{L^{py}}$) in the electrocatalytic HER. In the ligand series, a heterocyclic donor group by the 2-pyridyl function is systematically changed. This small structural feature is expected to define the predominant equilibrium species in solution and affect the stabilization of the reduced complex forms. Indeed, earlier studies suggested that catalytic oxidations by Fe(II) pre-catalysts containing the $\mathbf{L^{O/S/NH}}$ ligand series exhibited activity and stability of the corresponding oxidized species depending on the systematically varied, non-coordinating heteroatom [1,2].
The complexes were isolated and analyzed as solids by known procedures [1]. Electrochemistry was performed in a 3-electrode cell, using a glassy carbon working electrode, under argon. Hydrogen production during controlled potential electrolysis in an H-cell was quantified by GC. Solution equilibria were analyzed by UV-vis spectroscopy, or electrochemistry upon titration of the complex with the ligand, or trifluoroacetic acid.
We found that the differences in the reduction potentials of the compounds in acetonitrile correlate with the basicity of the ligands. The addition of trifluoroacetic acid as proton source suggested that the Fe(II) $\mathbf{L^{S/O/NH}}$ complexes act as homogeneous catalysts in the HER. Kinetic studies and controlled potential electrolysis were used to explore the structure-activity relationships. The catalytic activity could be associated with the $\mathrm{Fe}(\mathbf{L^{S/O/NH}})_2^{2+}$ structural moiety. In contrast, the complex with $\mathbf{L^{py}}$ was inactive in catalysis, due to the persistence of the low spin $[\mathrm{Fe}(\mathbf{L^{py}})_3]^{2+}$ species in the reaction mixture. As shown by our findings, the differences in the redox behavior of the compounds correlate with the basicity of the ligands that in turn depend on the non-coordinating O/S/NH function.

Acknowledgements
This work was supported by the National Research, Development and Innovation (NRDI) Fund of Hungary (Hungary); grant numbers NKFI-128841 and TKP2021-NKTA-05. We also thank the Renewable Energy National Laboratory (Hungary) for support, financed by the RRF-2.3.1-21-2022-00009 project.

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Edge sites of MoS_2 catalysts are active for both HDS and HER reactions: the proof of concept

L. A. Zavala-Sanchez[1], K. Kumar[3], V. Martin[3], F . Maillard[3], X. Portier[2], F. Maugé[1], L. Dubau[3] and L. Oliviero[1]*

[1] *Laboratoire Catalyse et Spectrochimie, Normandie Université, ENSICAEN, UNICAEN, Caen, France*

[2] *Centre de recherche sur les Ions, les Matériaux et la Photonique, Caen, France*

[3] *Univ. Grenoble Alpes, CNRS, Grenoble INP, Univ. Savoie Mont Blanc, LEPMI, Grenoble, France*

[*] *laetitia.oliviero@ensicaen.fr*

Introduction. Since the pioneer work of Jaramillo et al. in 2007[1], MoS_2 has been considered promising to replace platinum (Pt) for the Hydrogen Evolution Reaction (HER) electrocatalysis. If the activity of MoS_2 has been linked with the total edge site concentration for both hydrotreatment reactions and HER reaction, no evidence has been given yet that well-performing MoS_2 catalysts for hydrotreatment reactions could lead to improved HER catalysts as well. In this study, we compare the thiophene hydrodesulfurization (HDS) and HER activities of a series of MoS_2 catalysts prepared with or without citric acid (CA) and with or without cobalt (Co) or Pt single atoms as promoter.

Experimental/methodology. Three series of mono- bi- and trimetallic (MoS_2/C, Co-MoS_2/C and Pt1%-$CoMoS_2$/C) catalysts with different amounts of CA were prepared by an incipient wetness impregnation method[2]. The thiophene HDS tests were carried out within a differential glass reactor at 623 K. Electrochemical measurements were carried out using a bi-potentiostat (Autolab PGSTAT302N) with a catalyst loading of 300 μg_{powder} cm^{-2}.

Results and discussion. The comparison between the activity in thiophene HDS and HER on MoS_2 catalysts (Figure 1) reveals that for both reactions the addition of CA is beneficial on the three composition series up to an atomic ratio of CA/metal of 2. This positive effect could be linked to a decrease in slab length as revealed by High Angle Annular Dark Field Scanning Transmission Electron Microscopy. The introduction of Co or (Co+Pt) further increases the activity towards both reactions, the best catalyst being Pt1%-$CoMoS_2$/C prepared with the atomic ratio of CA/metal of 2. This parallel in activity ranking is in agreement with active sites being the same for both reactions, providing rational guidelines on how to improve the HER activity.

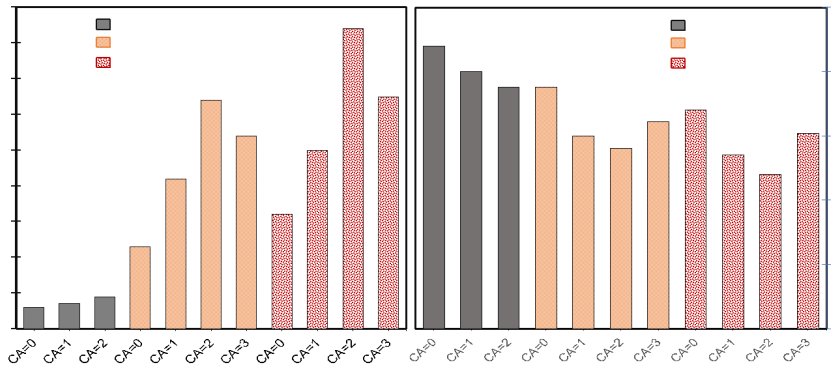

Figure 1. Effect of promotion and citric acid addition in MoS_2/C activity for HDS and HER reactions.

Finally, the dissolution of Mo, Co, and Pt elements during HER was monitored *in situ* using an eletrochemical flow cell connected to an inductively coupled mass spectrometer for the best-tested catalyst. Mo dissolves, particularly in the first cycles in agreement with the leaching of partially sulfided Mo entities[2]. Thus, improving the Mo sulfidation degree should lead to more stable catalysts.

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Electrosynthesis of ammonia with high selectivity and high rates via engineering of the solid-electrolyte interphase

Shaofeng Li*, Jens K. Nørskov*, Ib Chorkendorff*

Department of Physics, Technical University of Denmark, Kongens Lyngby, Denmark

Keywords: ammonia, electrosynthesis, SEI, high selectivity, high rates

Introduction. Ammonia (NH_3) is one of the most abundantly produced chemicals, with an annual production exceeding 182 million tonnes.[1] Currently, the only known reliable method of electrochemical NH_3 synthesis at ambient temperature is lithium-mediated nitrogen reduction (LiNR).[2] Although the accurate mechanisms are still not entirely understood, it is broadly believed that this LiNR process relies on the metallic lithium reduced from Li^+ to dissociate N_2 followed by a sequence of electron and proton transfers to form NH_3 with suitable proton donors.[2] Our recent work has demonstrated 78% FE at a current density of -0.004 A cm_{geo}^{-2} achieved by adding 0.6 to 0.8 mol% oxygen to the 20 bar N_2 atmosphere, which is attributed to the modification of the solid-electrolyte interphase (SEI) layer formed between the active (lithium) surface and the electrolyte during operation.[3] To overcome the gap of low current density, we also proposed increasing the current density (e.g., -0.1 A cm_{geo}^{-2}) by the use of high surface area copper electrodes.[4] The challenge still remains to achieve high FE and a commercially relevant current density (i.e., around -1.0 A cm_{geo}^{-2}) in a single system.

Experimental/methodology. The electrochemical measurements were conducted with Bio-Logic SP-200. The produced NH_3 was quantified by colorimetric indophenol method. X-ray photoelectron spectroscopy (XPS) was conducted on a ThermoScientific Thetaprobe instruments with an Al Kα x-ray source and base pressure below 9.0×10^{-10} mbar. X-ray diffraction (XRD) patterns were recorded on a Malvern Panalytical Empyrean X-ray diffractometer ($K\alpha_1$ = 1.540598 Å). Our calculations are based on density functional theory (DFT) within the generalized Kohn-Sham scheme, using in the Vienna Ab initio Simulation Package (VASP).

Results and discussion. In this work[5], we systematically address this challenge by modifying the SEI layer and improving the accessible surface area (per geometric surface area) simultaneously. We concentrate on determining the dynamic changes of the SEI under different experimental conditions and understanding how the SEI layer improves the performance of the LiNR process by tuning the ionic conductivity. We study several electrolytes, and suggest that a fluorine-based electrolyte is the best. In combination with a highly porous Cu electrode, we demonstrate 95 ± 3% faradaic efficienct (FE) at a current density of -0.1 A cm_{geo}^{-2} under 20 bar N_2. In addition, we show a FE of 71 ± 3% is achievable at a current density of -1.0 A cm_{geo}^{-2}, delivering an NH_3 production rate of 2.5 ± 0.1 μmol s^{-1} cm_{geo}^{-2} (Figure 1B). The new results are attributed to the uniform lithium fluoride (LiF)-enriched SEI layer that facilitates even lithium deposition and suppresses the uncontrolled electrolyte degradation. The different SEI layers were characterized with XPS and XRD, where we confirmed the presence of lithium fluoride. Moreover, we also found that the produced NH_3 does not only exist in the electrolyte, but also in the gas phase and in the deposited layer with SEI, and the NH_3 concentration distribution in different phases is highly related to the lithium salt used.

Acknowledgments

We gratefully acknowledge the funding by Villum Fonden (V-SUSTAIN grant 9455), Innovationsfonden (E-ammonia grant 9067-00010B) and the European Research Council (ERC) CLUNATRA under the European Union's Horizon 2020 research and innovation program (grant agreement no. 741860).

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Application aspects of molten proton conductor fuel cell modules with internal methanol reformer

K. Kappis[1], Y. Li[2], J. Papavasiliou[1], H. Li[2], D.E. Vlachos[3] and G. Avgouropoulos[1*]

[1]*Department of Materials Science, University of Patras, Patras 26504, Greece*
[2]*State Key Laboratory of Ocean Engineering, School of Naval Architecture, Ocean and Civil Engineering, Shanghai Jiao Tong University, Shanghai 20400, China*
[3]*Pleioni Energy S.A, Patriarchou Grigoriou & Neapoleos Str, Ag.Paraskevi, 15310, Greece*
[*]*geoavg@upatras.gr*

Keywords: molten proton conductor, fuel cell, methanol reformer, hydrogen, copper catalyst

Introduction. A high-temperature proton exchange membrane fuel cell (HT-PEMFC) based on PBI doped with phosphoric acid (PA) can be functional between 120–200°C [1,2]. A traditional methanol reforming copper-based catalyst operates between 200 and 300°C. To address the mismatch of the operating temperatures between the fuel cell and the methanol reformer, the simplest and most efficient approach would be to develop a new type of fuel cell capable of working at above 200 °C. We have proposed the concept of internal reforming methanol fuel cell (IRMFC), where the methanol reformer is incorporated into the anode compartment of a HT-PEMFC. This system could effectively operate at 200–210 °C [1]. We have recently prepared a molten proton conductor electrolyte membrane (PBI membrane doped into molten $CsH_5(PO_4)_2$), with promising performance at 160–220 °C [2]. In the present work, we report on the performance of last generation IRMFC modules (reformers, single cells and stacks).

Experimental/methodology. IRMFC modules were designed, constructed, assembled and tested based on: (i) Combustion synthesized CuZn-based methanol refroming catalysts (mainly CuZnGaAlOx (CZGA) and commercial HiFUEL R120 catalyst (CuZnAlOx) as reference material) supported on the GDL of a carbon paper (catalyst loading = 100 mg/cm^2). (ii) $CsH_5(PO_4)_2$-doped polybenzimidazole (PBI) molten proton electrolyte membrane sandwiched between two gas diffusion electrodes (GDEs; Pt loading= 0.5 mg/cm^2) and MEAs active area of 10-27 cm^2; (iii) Au-coated Al plates (1 mm thickness; double serpentine flowfields). The integrated cells (1 cell and 4 cell modules) were tested at 160-220°C under various H_2/He and H_2O/MeOH feedstreams. An electronic load was employed for the collection of polarization curves were collected via an electronic load, while inlet/outled gas streams were monitored with a GC/MS system.

Results and discussion. This study demonstrated the functionality and the promising prospects of last generation of IRMFCs, where a molten proton conductor fuel cell (MPCFC) was integrated with a methanol steam reformer, and efficiently operated on hydrogen or reformate feed streams at 220 °C. Either the single cell or the cells of the stack, showed a stable electrochemical behavior, since a hydrogen-rich stream (>99.9% methanol conversions; <0.5% CO selectivity) was provided by the methanol reformer, resulting in a mean cell voltage of 0.7 V at 200 mA/cm^2 (220 °C), keeping an OCV >1 V, similarly with the corresponding runs under simulated hydrogen streams. All the modules were tested over a period of 1 month including startup/shutdown cycles. Humidifcation of the anode feedstream was favorable in order to avoid dehydration of the electrolyte, while observed degradation was also attributed to the proton conductor loss in CL (EIS and CV analysis), a behavior that has been improved with last generation membranes [3].

Acknowledgments

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CO_2 Electroreduction on Bimetallic Au-Cu_2O Catalysts

Bianca Ligt[1*], Marta Costa Figueiredo[1,2], Emiel J.M. Hensen[1]

[1]*Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands*
[2]*Eindhoven Institute of Renewable Energy Systems (EIRES), Eindhoven University of Technology, Eindhoven, The Netherlands*

**E-mail corresponding author: b.ligt@tue.nl*

Keywords: CO_2 electroreduction, copper oxide, ethylene, ethanol

Despite its promising performance for C_{2+} product formation in electrochemical reduction of CO_2 (CO_2RR), Cu-based catalysts exhibit a relatively poor selectivity towards important chemical intermediates such as ethylene and ethanol. Up to 16 different products can typically be formed during CO_2RR.[1] Cu is the only element that can form C-C bonds at an appreciable rate.[2] Therefore, it is critical to better understand the active sites of Cu-based electrocatalysts, as it can lead to better catalyst design with improved selectivity towards desired products. A common approach is to investigate the reactivity of well-defined surface terminations of Cu, which can be achied by employing shape-controlled (nano)particles.[3] Here, we expanded on such studies by evaluating the impact of Au on well-defined Cu_2O surfaces for the electrochemical reduction of CO_2. This promoter metal was chosen, because it can reduce CO_2 to CO, which is widely accepted as the key intermediate for C-C coupling.[2,4]

In this study, Cu_2O nanocubes that predominantly expose the (100) facet were synthesized with a ligand-free method. The (100) facet is more active in the production of ethylene at the expense of unwanted methane formation, which takes place predominantly at the (111) facet.[3] The surface of the nanocubes was decorated with Au nanoparticles, as can be seen from the TEM images in **Figure 1**. The electrocatalytic tests were done in a range of potentials in neutral electrolyte (0.1 M $KHCO_3$). With Au as promotor, we found that more CO is formed, which can facilitate the formation of C_{2+} products. The nanostructured catalysts were (electrochemically) characterized prior to and after CO_2RR, leading to valuable insights in the differences in activity and morphology.

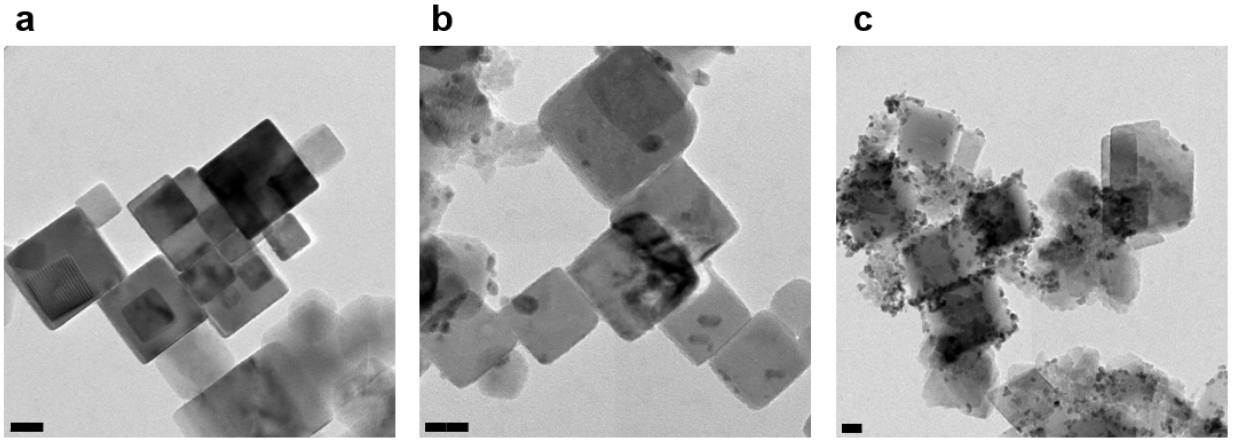

Figure 1. TEM images of **a**, Cu_2O, **b**, 1Au/Cu_2O and **c**, 5Au/Cu_2O. The scalebars correspond to 20 nm.

Acknowledgements
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Multicarbon Products by CO_2 Electroreduction Using Polarized Nickel Catalysts

Y. Zhou[1], A. J. Martín[2*], F. Dattila[3], S. Xi[4], P. Preikschas[2], N. López[3], J. PérezRamírez[2], B. S. Yeo[1]

[1] *National University of Singapore, Singapore*
[2] *ETH Zürich, Zürich, Switzerland*
[3] *Institute of Chemical Research of Catalonia, Tarragona, Spain*
[4] *Institute of Chemical and Engineering Sciences, A*STAR, Singapore*
[*] *antonio.martin@chem.ethz.ch*

Keywords: CO_2 electroreduction, nickel catalysts, long-chain products.

Introduction. Despite an intense catalyst search lasting for more than three decades, to date, only copper-based catalysts have been known to generate multicarbon products in CO_2 electroreduction at appreciable rates and are mostly limited to ethylene and C_2-C_3 oxygenates.[1]

Experimental. Catalyst evaluation was performed on gas diffusion electrodes. Structural properties under reaction were assessed by X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS). CO adsorption strength was evaluated by CO stripping. Mechanistic aspects were studied by reduction of selected compounds and density functional theory (DFT) simulations.

Results and discussion. We disclose herein that catalysts derived from inorganic nickel oxygenates (INOs), herein exemplified for the best performer phosphate-derived nickel (PD-Ni), can generate 29 products including up to C_6 hydrocarbons and C_4 oxygenates with relevant Faradaic efficiencies (FE).[2] Sustained operation yielded ca. 12% FE for C_{2+} products (**Fig. 1a**). The distribution of the predominant hydrocarbons closely fitted the Anderson-Schulz-Flory (ASF) distribution (**Fig. 1b**). The unique feature of these materials is the presence of stable, polarized $Ni^{\delta+}$ sites observed by operando XANES (**Fig. 1c**) and associated to Ni-O bonds via operando EXAFS, which can bind CO moderately as revealed by CO stripping analysis (**Fig. 1d**). Mechanistic studies on PD-Ni suggest that $Ni^{\delta+}$ sites favor a path reminiscent of the Fischer-Tropsch process where COOH + CH_x coupling is followed by CH_x insertions. Advanced product quantification enabled us to identify performance trends arising from variation of key operation parameters (*e.g.*, electrolyte pH). Our results unlock the latent reactivity of polarized nickel to give access to a broader pool of valuable products.

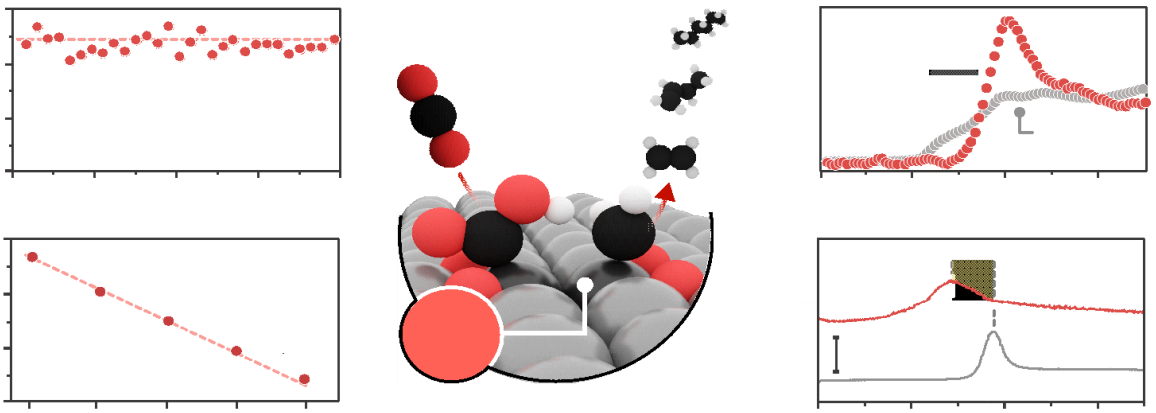

Figure 1. (a) FE for C_2-C_6 products. (b) Fitting of the hydrocarbon distribution to the ASF model. (c) Observation of polarized Ni sites in PD-Ni by operando XANES. (d) Milder CO adsorption strength on PD-Ni by CO stripping analysis.

Acknowledgments

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Use of novel carbonaceous materials in mixed oxide-carbon composite supported Pt catalysts for polymer electrolyte membrane fuel cells

I. Ayyubov[1,2], E. Tálas[1*], I. Borbáth[1], Z. Pászti[1], C. Silva[1], M. Florea[3], Á. Szegedi[1], S. Yazici[4], A. Tompos[1]

[1]*Research Centre for Natural Sciences, Eötvös Loránd Research Network (ELKH), Budapest, Hungary*
[2]*Budapest University of Technology and Economics, Budapest, Hungary*
[3]*National Institute of Materials Physics, Magurele, Romania*
[4]*Istanbul Technical University, Istanbul, Turkey*
[*]*talas.emilia@ttk.hu*

Introduction. Polymer electrolyte membrane fuel cells (PEMFC) convert chemical energy into electricity in an efficient and environmentally friendly way. Electrocatalysts are the primary elements of PEMFCs. The most commonly used commercial PEMFCs electrocatalyst, the carbon supported platinum (Pt/C), is known to suffer from electrocorrosion and is not resistant to CO poisoning. In our previous studies conducted in a three-electrode electrochemical cell, higher stability and CO tolerance was demonstrated for mixed oxide - carbon $Ti_{(1-x)}Mo_xO_2$-C (C= Black Pearls 2000 (BP), Vulcan XC-72) composite supported Pt electrocatalysts compared to commercial Pt/C [1]. Due to their conductivity, stability, and high specific surface area (SSA), novel carbonaceous materials such as carbon nanotubes, graphene, graphene nanoplatelets (GNP) offer new solutions for above catalysts in both hydrogen oxidation and oxygen reduction reactions. Present work aimed the study of composite supported catalysts from graphene derivatives.

Experimental/methodology. 75 wt. % $Ti_{0.8}Mo_{0.2}O_2$-25 wt. % C type of composites were synthetized by multistep sol-gel method followed by high temperature heat treatment in Ar (HTT, 600°C, 8 h) [1]. Graphite oxide (GO), GNP and their mixture were used as starting carbonaceous materials. For comparison, BP based samples were also prepared. The effect of a solvothermal treatment step before the HTT was also studied. The composites were characterized by Raman spectroscopy, XRD, SEM, TEM and XPS. Pt nanoparticles (20 wt. %) were loaded on the composite supports by ethylene glycol-$NaBH_4$-assisted reduction [1]. Metal content was measured by ICP; SSA was obtained by N_2 physisorption. The electrical conductivity (σ) was estimated by use of impedance spectroscopy. Electrochemical performance was evaluated by polarization curves, cyclic voltammetry, and rotating disc electrode measurements.

Results and discussion. The new type of electrocatalysts contained the mixed oxide in rutile phase; no separate Mo-oxides were observed (Fig. 1A). In all samples, Pt existed in a highly dispersed form with an average particle size of 3-4 nm. Electrochemical surface area (ECSA) was calculated from cyclic voltammograms, and the long-term stability of the samples was expressed as $ECSA_N/ECSA_1$ values (N: number of cycles). Stability of our electrocatalysts was higher than that of commercial Pt/C (Fig. 1B).

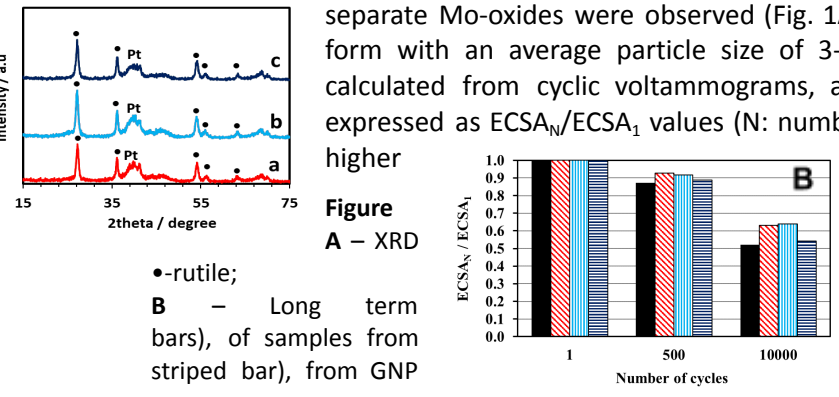

Figure 1. Characterization of the electrocatalysts. **A** – XRD patterns of samples from BP (a), GO (b), GNP (c), •-rutile; **B** – Long term electrochemical stability of reference Pt/C (solid bars), of samples from BP (diagonally striped bar), from GO (vertically striped bar), from GNP (horizontally striped bar)

The electrocatalytic properties of Pt catalysts supported by the novel composites will be correlated with their structural features in the lecture.

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Influence of the upper potential limit on the stability of PtRu catalysts for reformate PEMFCs during potential cycling-based anode ASTs

V.Berova[1], K. Hengge[1], T. Burger[1], C. Scheu[2], T. Jurzinsky[1*]

[1]*Freudenberg Fuel Cell e-Power Systems GmbH, München, Germany*
[2]*Max Planck Institut für Eisenforschung GmbH, Düsseldorf, Germany*
[*]*tilman.jurzinsky@freudenberg-eps.com*

Keywords: accelerated stress test, platinum, ruthenium, stability, CO tolerance

Introduction

Pt Ru catalysts are well-established anode catalysts for reformate operated proton-exchange membrane fuel cells (PEMFCs). The addition of Ru as a co-catalyst mitigates the CO poisoning of Pt sites due to its promoting effect towards CO-oxidation [1]. However, Ru is more susceptible to dissolution and thus less stable than Pt [2]. Therefore, major efforts must be taken to improve the durability of PtRu catalysts to enable long PEMFC lifetimes. Potential cycling-based accelerated stress tests are commonly employed to investigate the stability of electrocatalysts with little time and costs.
In this study, the effect of the potential on the degradation of a PtRu catalyst is investigated. For this purpose, several AST protocols based on square cycling the anode potential for 30000 cycles with varying upper potential limit were developed and tested on cells with the same material composition.

Experimental

The ASTs were used to test a carbon-supported PtRu catalyst in a membrane electrode assembly (MEA) setup. The PtRu anodes were manufactured in-house with a patented technique [3], while for membranes, cathode catalysts, and GDLs commercially available products were applied. Before, during, and after the AST, electrochemical characterization was conducted via cyclic voltammetry, CO-stripping, and recording U-I curves. After the AST, post-mortem analyses were performed by means of transmission electron microscopy, X-ray diffraction, and cross-sectional scanning electron microscopy coupled with energy dispersive X-ray spectroscopy to analyze the prominent degradation mechanisms occurring for the different testing conditions.

Results and discussion.

The upper potential limit showed strong influences on the degradation of the anode and consequently on the MEA. At potentials below 0.2 V_{RHE} no significant Ru dissolution could be observed. With increasing the potential from 0.65 to 0.8 V_{RHE}, the severity of Ru dissolution increased resulting in a reduced CO-tolerance. At the same time, the consequent Ru crossover from anode to cathode, poisoning the cathode rose with increasing upper potential limit. By further raising the potential, additionally severe Pt dissolution occurred, which ultimately led to a drastically lowered electrochemical active surface area (ECSA) on the anode and thus overall cell performance.
Future work will address the correlation of these ASTs to long-term testing at constant potential.

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Porous Nickel Nanostructure Coupled with Localized Electrochemically Induced pH Tuning for Sensitive and Selective Nonenzymatic Glucose Detection

Clara Ehinger[1,2], Jérémie Gouyon[1*], Su Ha[2], Alain Walcarius[1]

[1] *Université de Lorraine, CNRS, LCPME, F-54000 Nancy, France*
[2] *Washinton State University, Voiland School of Chemical and Bio Engineering, Pullman, USA*
[*] *jeremie.gouyon@univ-lorraine.fr*

Keywords: glucose detection, electrochemical oxygen filter

Introduction. Glucose detection is essential in industries including food production, viticulture, pharmaceuticals, and diagnostic medicine, such as the treatment of diabetes. Further, demand for fast, reliable, sensitive, and selective glucose sensors continues to grow. For example, by 2030, more than 5.4% of the global population, 366 million people, are expected to be affected by diabetes[1]. Enzymatic methods currently dominate, although growth in demand and scientific advancements have prompted the development and improvement of non-enzymatic detection methods[2]. Compared to enzymatic methods, non-enzymatic sensors are simpler to produce and implement and show potential to be more selective towards glucose. Previous research has shown many potentially viable methods of non-enzymatic glucose sensors[2,3], including Ni-based catalysts. However, these glucose sensors only work in highly alkaline environments which is not conducive to in situ measurements. Therefore, a novel glucose sensor is proposed which implements an electrochemical pH tuner in a four-electrode electrochemical setup. The purpose of the additional electrode is to reduce water into OH^- species, increasing the pH locally, only around the Ni catalyst, providing a sufficiently alkaline environment for precise measurements.

Experimental/methodology. Electrode preparation was performed using a three-step electrochemical synthesis process in a three-electrode setup. Electrodeposition of a Ni-porous catalyst from a $NiCl_2$ precursor was first optimized on glassy carbon,[3] and then applied to a gold microelectrode. Hydrogen bubble formation during Ni deposition was exploited to create the porous Ni nanostructure. $NiCl_2$ concentration, deposition time and deposition current were optimized for the greatest glucose sensitivity using cyclic voltammetry and chronoamperometry. The glucose detection measurements were done in alkaline solutions. Due to the need of a high pH, in situ measurements of glucose are not possible with the proposed three-electrode setup. To solve this, an additional porous electrode (initially developed as "electrochemical oxygen filter"[4]) was included in the system as a second working electrode thus allowing glucose to be detected in less alkaline environments.

Results and discussion. A nanostructured Ni catalyst electrode successfully detected glucose at varying concentrations. Parameters optimized for the highest glucose sensitivity were applied when preparing the nanostructured Ni catalysts on a microelectrode. Coupling the Ni catalyst electrode with an additional porous cathode in a four-electrode setup was found to increase selectivity during in-situ glucose detection tests by increasing the pH of the environments. The successful demonstration of nanostructured Ni catalysts coupled with localized pH increase by electrochemically induced production of hydroxide species indicates that this method is a viable candidate for implementation and scale-up testing. This glucose detection paradigm has the potential to increase accuracy and decrease costs in lifesaving glucose testing.

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Influece of Lithium on Phase Transition of Amorphous Iridium Oxohydroxide for Oxygen Evolution Reaction.

M. Falsaperna,[1] S. J. Freakley[1]

[1]*University of Bath, Bath, United Kingdom*
[*]*sf756@bath.ac.uk*

Introduction. Electrolysis is one of the most promising methods for the production of hydrogen *via* water splitting. However, the sluggish oxygen evolution reaction (OER) leads to cell overpotentials higher than the thermodynamic value, 1.23 V_{RHE}, with energy losses up to 53%.[1] While iridium oxide, IrO_2, has proven to be one of the most promising materials to achieve OER in acidic media, obtaining catalysts with lower overpotentials is still necessary, with a focus on the fine balance between activity and stability. Synthesising $Ir(O)_x(OH)_y$ in the presence of alkali metal salts has been shown to affect the morphology and composition of the catalyst surface, with an effect on its electrocatalytic properties.[2] We have developed a facile synthesis method to produce nanocrystalline lithium iridate, Li_2IrO_3. This material has shown remarkable activity and stability towards OER, with the former comparable to that of amorphous $Ir(O)_x(OH)_y$, breaking the delicate relationship between high activity and low stability.

Experimental/Methodology. Our novel approach allows for the synthesis of nanocrystalline Liintercalated iridium oxide, Li-IrO_x, *via* heat treating amorphous $Ir(O)_x(OH)_y$ (500°C, 3 hours), previously obtained in the presence of Li_2CO_3 following a procedure described by Esquius *et al.*[2] The product is then washed with 1 L cold and 1 L hot water and left to dry in open air. Linear scanning voltammetry (LSV) and chronopotentiometry (CP) are used in a 3electrode setup containing 0.1 M $HClO_4$ electrolyte to investigate the electrocatalytic activity and the stability of the catalyst, respectively. The material was characterised using XRD, STEM, *operando* XAS and XPS.

Results and discussion. Following the synthesis of the amorphous $Ir(O)_x(OH)_y$, residual Li^+ is shown to suppress the formation of rutile IrO_2 upon thermal treatment and leads to a transition to a nanocrystalline Li-layered iridium oxide, whereas the removal of residual Li^+ results in the formation of rutile IrO_2 (**Figure 1a**). High resolution aberration corrected transmission electron microscopy shows the lithiumintercalated iridium oxide is polycrystalline with nanocrystalline domains. The Li-intercalated phase shows electrocatalytic activity comparable to amorphous iridium oxide while exhibiting a remarkable stability, similar to that shown by rutile IrO_2 (**Figure 1b** and **1c**). These results suggest the incorporation of metal alkali in the structure of the catalyst leads to improved stability while retaining significant activity towards OER, potentially offering the opportunity to produce highly active and durable electrocatalysts for industial applications.

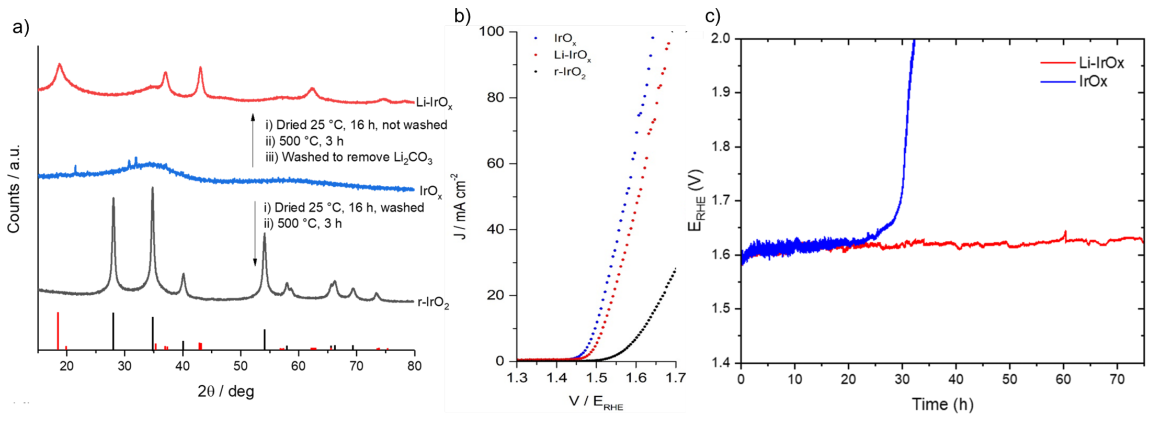

Figure 1. a) XRD pattern (Cu K_α = 1.5046 Å) of amorphous IrO_x heat treated in the presence\absence of residual Li^+. Black and red references patterns of rutile IrO_2 and β-Li_2IrO_3, respectively. b) LSV (1.2-1.7 V_{RHE}, 5 mV s^{-1}) of IrO_x, Li-IrO_x and rutile IrO_2 and c) Stability of Li-IrO_x and IrO_x (CP, 10 mA cm^{-2}, 75 h).

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Noble metal-free anode fuel cells for portable devices

S. Neațu[1], F. Neațu[1], S. Somacescu[2], V. Șomoghi[3], M. Florea[1*]

[1]*National Institute of Materials Physics, Magurele, Romania*
[2]*"Ilie Murgulescu" Institute of Physical Chemistry,Romanian Academy, Bucharest, Romania*
[2]*Stimpex S.A., Bucharest, Romania*
[*] *mihaela.florea@infim.ro*

Introduction. As the price of oil has climbed fivefold from 1990 to the present, it is clear that our dependence on energy sources is unsustainable in light of rising energy consumption and the accompanying depletion of fossil fuel deposits [1]. There are challenges to using renewable energy, at least in its most frequent forms now. Common renewable energy technologies rely on the sun, wind, or fuels, all of which have drawbacks in terms of reliability, quantity, and even environmental friendliness. In this light, fuel cells are, and will continue to be, among the most efficient and reliable methods of generating electricity from renewable sources. Polymer Membrane Electrolyte Membrane Fuel Cells (PEMFCs) convert chemical energy directly and efficiently into electricity and water as the only by-product. However, for this to be accomplished in a productive manner, these PEMFCs require very efficient electrodes [2].

Advances in fuel cells and renewable fuel use alternatives have rekindled interest in portable fuel cells in recent years. Their primary benefits include higher power densities per unit active area due to a simple anode reaction, and cleaner combustion, both of which are not present in competing for portable fuel cells. In response to these tendencies, a consortium composed of two academic institutions and a business economic actor has set out to construct ethanol-fueled, noble metal-free anode fuel cells for portable devices within the next several years. However, this is only the beginning of our collaboration; much more work has to be done on the project. Consequently, only results from the initial period are shown here.

Experimental/methodology. In this work, different Ni/SnO_2 materials were produced using a literature-documented synthesis method [3]. In short, the hydrothermally generated SnO_2 materials are utilized as supports for Ni-based electrocatalysts. The deposition-precipitation process was used for this aim. Thus, a nickel inorganic salt (nickel(II) chloride hexahydrate) was dissolved in Milli-Q water, and then *in situ* reduction of Ni nanoparticles with hydrazine monohydrate was performed at room temperature while using vigorous magnetic stirring. Then, the desired amounts of mesoporous SnO_2 were added to create the final products containing different concentrations of Ni. In order to characterize these composites, a number of different techniques, including TG-DTA, XRD, SEM, TEM, textural analysis (BET), Raman and X-ray photoelectron spectroscopies, were utilized in this study. These Ni/SnO_2 were then mixed with carbon-based powders available for purchase to create electrodes via an electrospray deposition method. The electrode depositions were done with a homemade tool developed for that specific reason. The finished cell's cathode was made out of commercially available Pt/C electrodes.

Results and discussion. A reliable and consistent performance (peak power density ~35 mW cm^{-2} obtained at 90 °C) of the final cell fueled with ethanol can be attained with the as-prepared anode materials due to their (*i*) high porosity suitable for ethanol transport, (*ii*) sufficient electronic conductivity, (*iii*) chemical stability and high C and CO tolerance (ensured by well-defined chemical states that do not undergo major changes) in a reducing fuel atmosphere, (*iv*) compatibility with other ethanol fuel cell components, (*v*) ease of fabrication, and most importantly (*vi*) low cost. As a result of our initial stage research, we conclude that using Ni/SnO_2-based anodes in the development of our industrial prototype (hence referred to as BEC) has the potential to be a game-changing technique for generating electricity in the future.

Acknowledgments
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Electrochemical ammonia synthesis via nitrogen reduction coupled with hydrogen oxidation in a continuous-flow reactor

Xianbiao Fu,[1] Ib Chorkendorff[1]*

[1] *Department of Physics, Technical University of Denmark, Kongens Lyngby, Denmark.*
**Corresponding Author's E-mail address: ibchork@fysik.dtu.dk*

Keywords: lithium-mediated nitrogen reduction, flow cell, hydrogen oxidation

Introduction. Ammonia (NH_3) is an important chemical for society to produce fertilizers, pharmaceuticals, polymers, and other chemicals. Electrochemical ammonia synthesis is regarded as a promising route to complement the Haber-Bosch process for the distributed production of fertilizers in small-scale devices powdered by renewable electricity.[1] After rigorous quantitative (*i.e.* gas purification and quantitative isotope measurements) investigations, lithium-mediated nitrogen reduction reaction (Li-NRR) was validated as the only currently reliable route for electrochemical ammonia synthesis.[2,3] Although significant progress has been made to achieve high FE and current density[4,5], most Li-NRR studies have the limitations of sacrificing solvent as protons for ammonia synthesis and difficulties in scaling up production in batch-type electrochemical cells (*i.e.*, one-compartment cells and autoclaves).

Experimental/methodology. Here, lithium-mediated electrochemical ammonia synthesis was carried out in a three-chamber flow cell at 1 bar and the effective area of the flow field was 25 cm^2.[6] The stainless-steel cloth (SSC) with a pore size of 30 μm was used as a gas diffusion electrode (GDE) to overcome the mass transport limitation of N_2 and H_2. The PtAu alloy catalysts on the SSC substrate (PtAu/SSC) were used for hydrogen oxidation reaction (HOR) at the anode side. The solution of 1 M lithium tetrafluoroborate ($LiBF_4$) in THF contained varying concentrations of 0 to 1 vol. % ethanol as an electrolyte. A syringe pump was used to flow the electrolyte with 1 ml/min flow rate.

Results and discussion. We here show that the classical catalyst Pt does not work for stable HOR (deactivated in a few minutes) in the organic electrolyte, while PtAu alloy is essential for reducing the anode potential (anode potential: 0.6 V, cell voltage: 4.3 V) avoiding the decremental decomposition of the organic electrolyte. The PtAu alloy demonstrated long-term stability and high activity of HOR in the Li-NRR organic system. *Operando* mass spectrometry of deuterium (D_2) oxidation demonstrated that hydrogen oxidation can continuously provide protons for ammonia synthesis and confirmed the recyclability of ethanol as a proton shuttle. Benefitting from the robust PtAu anode catalysts, the potential cycling method and trade-off strategy of the proton/nitrogen limited region, record high faradaic efficiency of up to 61% and energy efficiency of 13% were achieved at 1 bar of nitrogen.

Acknowledgments

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Polymer monomer enhanced electrocatalysts for hydrogen and oxygen evolution in alkaline water splitting

Tzu Hsuan Chiang*, Hsin-Hsiang Hsieh

Department of Energy Engineering, National United University, Miaoli, Taiwan

**thchiang@nuu.edu.tw*

Abstract

Enhancing hydrogen production and efficiency from renewable energy sources such as solar cells, wind, and hydro-energy combined with water electrolysis [1] is a positive development for many investigations. Due to alkaline water electrolysis (AWE) has the advantages of using non-noble metal catalysts, low concentration of 30-40% KOH electrolyte, and providing high long-term stability [2]. The study prepared a bifunctional electrocatalyst as FeCuMo-Schiff base. The electrocatalyst was prepared from a mixture of poly (methyl methacrylate), metal precursors (Fe, Cu, and Mo), and a Schiff base. They were then using electrophoresis to coat on nickel foam. This study is focused on different amounts of PMMA contact with the metal Schiff base. It used a kind of polymer monomer as poly (methyl methacrylate) to enhance the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in alkaline water splitting. The results obtained 50 mg of PMMA added that can enhance HER and OER performance of the $Fe_{0.5}Cu_{0.5}Mo_{0.5}$-Schiff base, as shown in Fig. 1. The HER and OER electrocatalytic activities in alkaline water splitting are also better than the commercial electrocatalysts 20 wt% Pt/C and RuO_2.

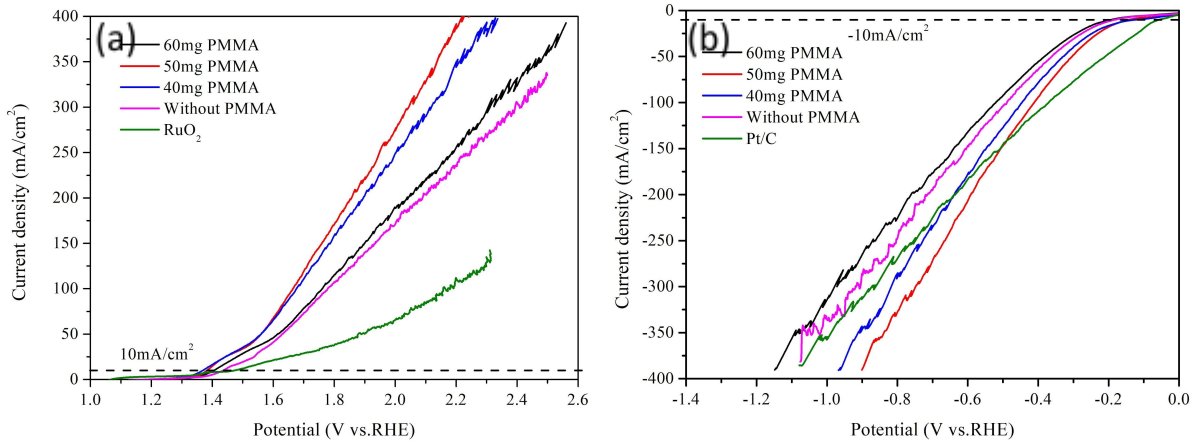

Figure 1. Polarization curves of (a) OER and (b) HER for Fe0.5Cu0.5Mo0.5-Schiff base content with different amounts of PMMA monomers.

Acknowledgments

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Catalysis of Anode Materials for Direct Ammonia Fuel Cell

Andrew C. Chien[1,2*]

[1]*Department of Chemical Engineering, Feng Chia University, Taichung 40724, Taiwan*
[2]*Green Energy Development Center, Feng Chia University, Taichung 40724, Taiwan*
[*] *cyinchien@fcu.edu.tw*

Direct conversion of ammonia (NH_3) to hydrogen (H_2) in a fuel cell has the potential to realize a carbon-neutral world in transportation and distributed-power applications. Most fuel-cell research has involved the use of H_2 as the fuel; however, the practical generation and storage of H_2 remains an important technological hurdle. Ammonia is an alternative energy carrier not only with a high energy content but also with a facile condition to use. Nevertheless, degradation of anode materials occurs during operation, leading to performance loss and preventing this simple fuel in practical applications. Here we include lanthanum strontium ruthenium titanate (LSRT) into state of the art nickel cermet anodes and investigate catalytic activities of ammonia conversion in high temperature fuel cells. The cell performane is compared with two kinds of ceramic cells, one oxygn-ion conducting and another proton conducting, using NH_3 as a fuel. We demonstrate that presence of LSRT is beneficial to a proton-conducting cell with a high activity toward NH_3 conversion and a more structure stability during nitridation. Besides, a stable anode catalyst depends on an optimum metal-support interaction for dehydrogenation of NH_3 and subsequent associative N_2 desorption. Further studies are needed to understand the synergistic effect brought about by both metal and the support electrolyte. This will in turn allow to design an effective material capable of carrying out NH_3 cracking reactions for fuel cell and potential energy applications.

Keywords: Ammonia, fuel cell, nickel, LSRT, nitridation

Introduction.

Current ceramic fuel cells have received considerable attention for application in mobile and residential distributed power generation [1]. Most of them deliver stable performance using highly pure hydrogen (H_2) derived from fossil fuels via complex reactions and separation processes. Although H_2 is a promising clean fuel for energy production, its low volumetric density and high flammability pose a challenge in storage as well as transportation. Recently, ammonia (NH_3) has been regarded as a potential fuel source for a high energy density (~ 4 kWh/kg) and its safety to transport. Ammonia can be liquefied at a relatively facile temperature (20 °C) and a pressure (8.6 bar), yielding a higher volumetric density as compared to hydrogen. Traditional ceramic fuel cells capable of achieving high power densities are based on oxygen-ion conductors (Solid Oxide Fuel Cell; SOFC) operating at high temperatures (~ 800 °C). The high temperature operation not only allows a fast reaction kinetics in the SOFC without noble metals or precious catalysts but also make possible a direct conversion of ammonia into electricity.

Nevertheless, state of the art nickel anodes in high tmperature fuel cells experiences degradation when NH_3 is used as a fuel. In the past, alternative anodes have been attempted by doping or alloying the Ni cermet anode with another transition metal (M) such as Iron (Fe) and Chromium (Cr) [2]. The resulting Ni-M cermet is revealed to be an effective anode for NH_3 cracking and subsequent hydrogen oxidation. The incorporation of second metal promoted the anode durability via formation of metal nitride, thus suppressing the Ni agglomeration during operation. In the present work, we modify the Ni anode by doping with lanthanum strontium ruthenium titanate (LSRT) perovskite and study the effect of dopant. Catalytic properties of the LSRT for ammonia decomposition in a reactant gas simulating anode atmosphere are investigated. The addition of LSRT into the anode is beneficial to cell performance since exsolution of ruthenium (Ru) metal is expected to occur on the perovskite (LSRT) in a reducing atmosphere and Ru is an active NH_3-cracking catalyst. On the other hand, protonic ceramics (e.g. doped barium cerates) can conduct protons through their lattice with lower activation energies and higher ionic conductivities than the SOFC at

moderate temperatures at 600 °C. We incorporate the modified anode in a protonic ceramic fuel cells (PCFCs) and provided valuable information to design an effective anode material for a direct NH_3 fuel cell.

Experimental/methodology

Catalyst preparation

$BaZr_{0.2}Ce_{0.7}Y_{0.1}O_{3-\delta}$ (BZCY)

A protonic ceramic scaffold, $BaZr_{0.2}Ce_{0.7}Y_{0.1}O_{3-\delta}$ (BZCY), was synthesized and used as the electrolyte for a PCFC in this study. The synthesis was conducted by a solid-state reaction using precursors of barium carbonate (BaCO3, 99.8%), zirconium oxide (ZrO2, 99.9%), cerium oxide (CeO2, 99.9%), yttrium oxide (Y2O3, 99.9%) (All from Alfa Aesar) [3]. The precursors were weighed according to a stoichiometric molar ratio of Ba : Zr : Ce: Y = 1 : 0.2 : 0.7 : 0.1 and mixed in ethanol under ball milling. The mixture was then dried at 80 °C overnight and calcined at 1100 °C for 10 h. The obtained powder was crushed and grinded in the mortar for fabrication of an electrolyte.

Characterization

Catalytic activity on ammonia decomposition was evaluated by temperature-programmed reaction with an on-line mass spectrometer. Mass/electron ratio (m/e) in the MS were selected for H_2 (2), He (4), NH_3 (17), H_2O (18), N_2 (28), and O_2 (32). The phase composition of crystalline components on the catalyst was investigated by X-ray diffraction (XRD) analyses. The assignment of the various crystalline phases was based on the JPDS powder diffraction file cards. The morphology of the as-synthesized BZCY and LSRT catalyst was characterized by scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDX) and transmission electron microscope (TEM).

Results and discussion.

Figure 1 presents MS profiles of gaseous species from ammonia decomposition on different anode materials upon ramping temperature to 800 °C. The result shows that ammonia decomposes around 350 °C on all NiO-containing anodes while a complete conversion was achieved in the range of 550-800 °C (Also the conversion vs. temperature was plotted in supporting information, Fig. S1). Doping LSRT onto the anodes delayed the complete conversion, especially on the LSRT-NiO/YSZ, whose conversion temperature was raised to about 800 °C. On the other hand, H2 and N2 were the only gaseous products in the NH3 decomposition. The addition of LSRT not only caused a hump in the H2 MS profile at high temperatures but also produced a higher ratio of H2/N2 on both SOFC and PCFC anodes. For example, the ratio of H2 to N2 was increased from 2.0 (NiO/YSZ) to 2.3 (LSRT-NiO/YSZ) and from 1.6 (NiO/BZCY) to 2.4 (LSRT-NiO/BZCY), which was closer to 3, a theoretical value in NH3.

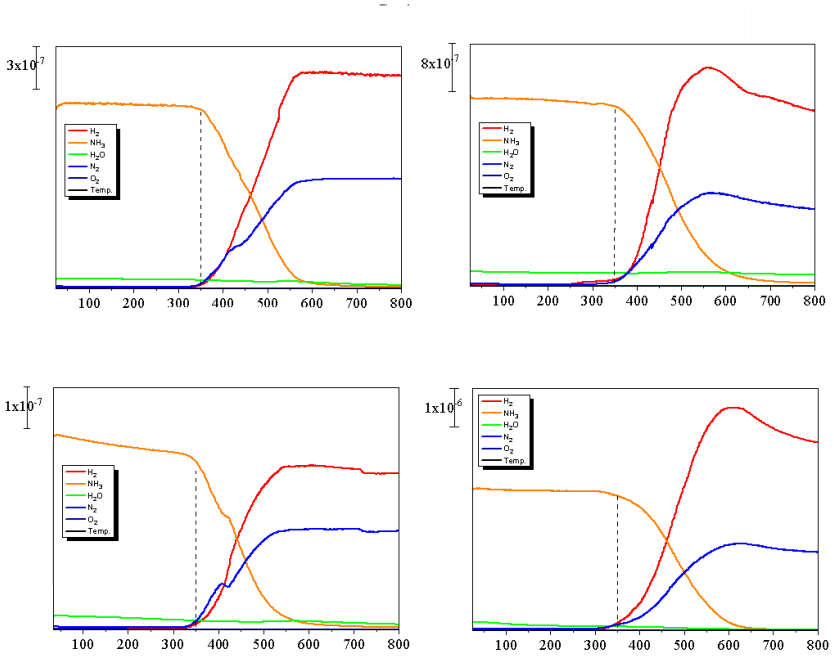

Figure 1 Temperature-programmed reaction activities of NH_3 decomposition on a) NiO/YSZ, b) LSRT-NiO/YSZ, c) NiO/BZCY, and d) LSRT-NiO/BZCY anode catalyst

Acknowledgments

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Simple and cost-effective surface modification for large area NiO electrode of Molten carbonate electrolysis cell

Yeeun Kim, Bo-Ram Won, Jae-ha Myung*

Department of Materials Science and Engineering, Incheon National University, Incheon 22012, South Korea
**Corresponding Author's E-mail address: mjaeha@inu.ac.kr*

Introduction. Molten carbonate electrolysis cell (MCEC) is one of the efficient and economical electrolysis technology for hydrogen production, because of the high operating temperature (600-650 °C).[1] However, facile coating technology for uniform nanocatalyst dispersion on large-area electrode sheets remains insuficient. In this study, we modified the surface of large area NiO electrode by decorating metal nanoparticles such as La and Co [2,3] uniformly via dip-coating, which is cost-effective fabrication procedure for the mass production. The porous NiO electrode sheets were fabricated by tape-casting and laminating process, and their porosity was controlled by adjusting ratio of pore former and laminating pressure. The electrode sheets were dip-coated into the suspensions including La and Co precursors and calcined to modify electrode surface. The oxide nanoparticles composed of each element on the electrode surface were observed. The amount of coated catalyst affected by ion concentration of the ions in suspensions and the number of dip-coating cycles. This study provides an insight for feasible strategy for customizing surface properties of the large-area electrode for hydrogen production.

Experimental/methodology. The porous and large area (100 cm^2) NiO electrode sheets were fabricated by tape-casting and laminating process. The tape-casting slurries with pore former of 15, 25, 35 wt% were prepared by two steps ball milling. The fabricated electrode sheets were cut into an appropriate size (5 cm^2) and dip-coated 1, 3, and 5 times into suspensions including La and Co precursors, respectively. The ion concentrations of the suspensions were 0.1 M and 0.5 M. The heat treatment was performed at 80 °C for 2 h after one cycle and finally at 500 °C for 3 h.

Results and discussion. The microstructures of electrode surfaces coated by different elements were investigated using SEM-EDS analysis. We evaluated catalyst content and coating homogeneity depending on ion concentration of suspension (0.1 M, 0.5 M) and cycle number of dip-coating (1, 3 and 5 times). Fig. 1 shows the surface of the electrode uniformly coated by nanoparticles of a granular form. The atomic fraction of Co was higher than that of La in all cases. The amount of catalyst (La, Co) coated on the electrode sheets was increased as the number of coating cycles and concentration of ions in suspensions increased. This indicates the amount of catalyst coated on the electrode can be controlled by the number of coating and ion concentration in suspensions.

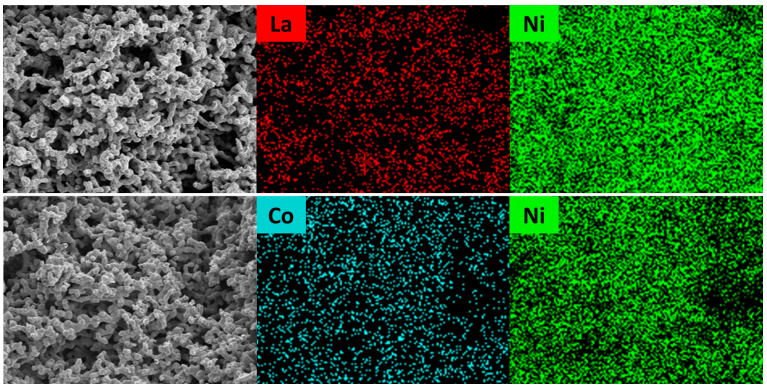

Figure 1 SEM micrographs of the surface of coated NiO electrode with corresponding EDS mapping.

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Controlling the growth of nanoparticles from exsolution modeling based on cation diffusion limitation.

Yo Han Kim, Somi Lee, Yeeun Kim, Jae-ha Myung*

Department of Materials Science and Engineering, Incheon National University, Incheon 22012, South Korea
**Corresponding Author's E-mail address: mjaeha@inu.ac.kr*

Introduction.

In-situ exsolution method has attracted much attention in preparation of supported nanoparticles as electrocatalysts. Unfortunately, growth of exsolved particles can be limited by diffusion, reactant and strain; Therefore, considerable metal atoms and cations remain in the inner bulk even under reduction condition at high temperatures. In this study, we suggest a diffusion-limited exsolution mechanism to control exsolution and overcome growth limitation. The endogenous nanoparticles in the reduced oxide were observed with an unbalance particle distribution, which is expected to be critical evidence of cation diffusion limitation. An exsolution model for particle growth was driven from the classical nucleation and diffusion theories, relating to cation concentration and reduction conditions. To demonstrate this model, we designed a titanate perovskite oxide system that can control the cation doping level. The exsolution trend depending on the Ni doping and reduction conditions corresponded with our modeling, providing insight for optimizing particle growth. Based on our experimental and theoretical results, we optimized the Ni exsolution on the electrode scaffold for solid oxide fuel cells. Single cells with an exsolable anode exhibited lower polarization resistance and higher power density than the undoped anode cell. In addition, an electrochemical switching technique leads to immediate enhancement of cell performance by applying an electrochemical potential, which promotes cation diffusion/exsolution.[1,2]

Methodology.

The modeling of exsolution phenomenon begins from Fick's laws of diffusion. The model based on an assumption in which the rate determining step of exsolution growth is cation diffusion toward the surface due to the fast reduction rate of cation.

Results and discussion.

The solution of Fick's second law is written as:

$$C(x,t) = C_0 \mathrm{erf}(x/2\sqrt{(Dt)}), \quad (1)$$

Where C is concentration and C_0 is initial concentration. x is the displacement and t is the reduction time. The diffusion in solid oxides is a thermally activated process as shown in Eq. 2.

$$D = D_0 \exp[-(E_a/RT)], \quad (2)$$

where D_0 is the maximum diffusivity, E_a is the activation energy for diffusion and R is the gas constant. The extent of exsolution (n_M) on the surface can be driven:

$$n_M = (2N_A C_0)\times\sqrt{(tD_0 \exp[-(E_a/RT)]/\pi}), \quad (3)$$

where N_A is the Avogadro's number. This theoretical result suggests that the extent of exsolution affected by the initial cation concentration, reduction time, and temperature, which are the key factors in controlling particle growth.

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Zeolite-templated synthesis of N-doped carbon using pyridine for the oxygen reduction reaction

S. Kokuryo[1*], K. Miyake[1], Y. Uchida[1], N. Nishiyama[1]

[1] *Graduate School of Engineering Science, Osaka University, Toyonaka, Japan*

Keywords: ORR, N-doped carbon, pyridine, zeolite

Introduction.

Recently, proton-exchange-membrane fuel cells (PEMFCs) have been expected as sustainable conversion systems of energy. However, the sluggish kinetics of oxygen reduction reaction (ORR) occurring at the cathode in PEMFCs restricts the cell performance[1]. Currently, Pt- and Ru-based catalysts are used commercially but are very expensive. Therefore, the development of low-cost and high-efficient catalysts for ORR has been desired. Recently, designing carbon-based electrocatalysts has been attractive as a promising candidate to solve the above problems. In particular, N-doped carbon materials have shown excellent activity for ORR[2]. It has been reported that edge Pyridinic-N sites on graphene are effective active sites. Herein, we synthesized N-doped zeolite-templated carbon using pyridine as C and N sources and investigated the activity for ORR.

Experimental/methodology.

In a typical carbon deposition process, 0.3 g of zeolites were heated under continuous He flows by raising the temperature to a certain carbon deposition temperature at an increasing rate of 10 K min^{-1}. Once the target temperature was reached, pyridine steam was carried by He gas for 6 h. Then, the obtained carbon-zeolite composites were treated with NaOH and HCl to remove the zeolite template. The obtained carbon product was washed with distilled water and dried at 90 °C, and then, they were calcined at 1100 °C under N_2 flow. The obtained catalysts were named Py-T (T is the carbon deposition temperature [°C]).

To evaluate the catalytic activity of the synthesized samples for ORR, Linear sweep voltammetry (LSV) measurements under alkaline conditions using 0.1 M KOH were conducted.

Results and discussion.

We observed that the crystallinity of zeolite decreased with increasing carbon deposition temperature. XRD measurements and EDX analysis confirmed that the zeolite template in every sample was almost completely removed after NaOH and HCl treatments. Rotating ring disk electrode voltammetry was used to evaluate the electrocatalytic activity of Py-T in the ORR. The catalytic activity and the selectivity of 4-electron direct reduction of O_2 to H_2O were found to enhance with increasing carbon deposition temperature, as shown in Fig. 1. However, the catalytic performance of Py-900 was slightly inferior to that of Py-800 because of the breaking of the zeolite structure during the high-temperature carbon deposition process.

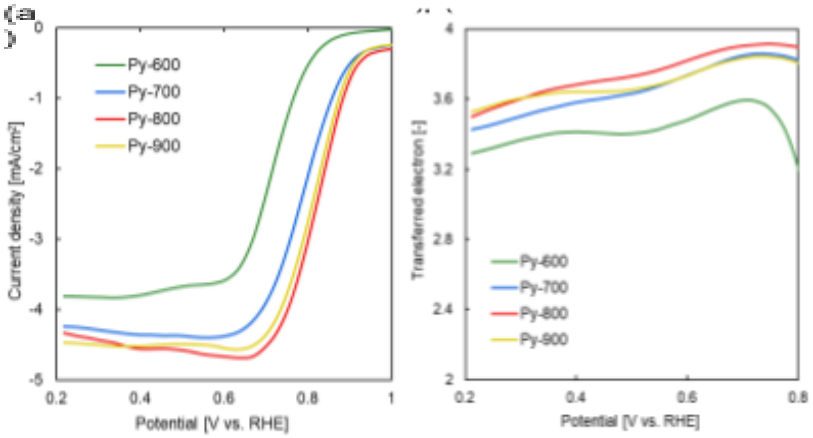

Fig. 1 (a) LSV curves, and (b) number of electrons transferred during ORR of Py-T.

Acknowledgments

Some experiments were conducted using a facility at the Research Center for Ultra-High-Voltage Electron Microscopy, Osaka University.

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Value-generating 5-HMF electrooxidation *via* a novel electrode at industrial current densities

M. L. Krebs[1], A. Bodach[1], C. Wang[2], F. Schüth*[1]

[1]*Department of Heterogeneous Catalysis, Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany*
[2]*Institute of Circular Economy, Faculty of Materials and Manufacturing, Beijing University of Technology, 100124 Beijing, P. R. China*
E-mail: schueth@kofo.mpg.de

Introduction. In conventional water electrolysis, the hydrogen evolution reaction (HER) is coupled with the oxygen evolution reaction, requiring high cell potentials while not generating any value. Coupling the HER with an electrochemical organo oxidation, e.g. HMF oxidation to FDCA, enables hydrogen production at lower cell potential while enabling the production of value-added products on the anode.[1] Realizing this, new electrode materials have to be developed to enable selective and efficient electrooxidation at current densities comparable to industrial HER.[2] We herein investigated the electrochemical oxidation of HMF as an exemplary reaction using a novel Fe-modified Ni-foam (NF) at industrial current densities.[3,4]

Experimental Fe-modified NF were prepared by treating a cleaned NF with a mixture of H_2O_2 and $FeCl_3$. Electrochemical measurements were performed using a Gamry Interface 1010 B electrochemical workstation with an H-type cell, which was separated by a Nafion 117 membrane. For more experimental details see Ref. 4.

Results and discussion. Modification of the NF with a mixture of H_2O_2 and Fe-precursors results in the formation and homogenous distribution of nanosheet-like structures on the surface of the Ni-foam. Combined analysis by XRD, XPS, and XANES, identifies those surface species as α-FeOOH and NiFe layered double hydroxide phases. Utilizing linear sweep voltammetry (LSV), current densities of up to 1 A cm^{-2} could be achieved by adding 100 mM HMF in 1 M KOH, demonstrating the potency of the as-prepared NF electrode. Constant potential electrolysis at 0.53 V vs. Hg/HgO and subsequent analysis with HPLC and NMR demonstrate FDCA yields beyond 90 % at faradaic efficiencies (FE) beyond 95 % while maintaining a well-closed carbon balance throughout the reaction. These results were maintained for 6 consecutive cycles, demonstrating the stability and reproducibility of this process. In addition, the performance of the electrode was tested in a flow H-cell configuration. Current densities of several 100 mA cm^{-2} could be maintained over a prolonged time when providing a sufficient supply of the organic substrate. Realizing that the instability of HMF in an alkaline electrolyte is a major challenge for industrial applications, we also investigated the alkaline degradation of HMF. At elevated alkalinity, the Cannizzaro reaction is the decisive degradation step of HMF, competing with humin formation. By optimizing the degradation conditions, ~80 % of the initial HMF could be maintained after the alkaline transformation to the Cannizzaro products (DHMF and HMFCA), which are both stable at elevated substrate and KOH concentrations. Constant potential electrolysis at 0.50 V vs. Hg/HgO confirms the simultaneous oxidation to FDCA. Furthermore, the stability of the Cannizzaro products allowed the "indirect" oxidation of HMF to FDCA at unprecedentedly high concentrations of substrate and base, 0.25 M and 5.0 M, respectively. Constant potential electrolysis enables the formation of FDCA at FE of ~95 % and yields of > 90 %, introducing both Cannizzaro products as stable HMF equivalents.

Acknowledgments
Financial support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy-Cluster of Excellence 2186 "The Fuel Science Center"- ID: 390919832 and FOR 2982-UNODE, Project number 413163866 is gratefully acknowledged.

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Towards higher NH_3 Faradaic efficiency: Selective-poisoning of HER active sites by co-feeding CO in NO electroreduction

M. Li[1], J. Verkuil[1], S. Bunea[1], R. Kortlever[2], A. Urakawa[1*]
[1]*Department of Chemical Engineering, Delft University of Technology, Delft, the Netherlands*
[2]*Department of Process & Energy, Delft University of Technology, Delft, the Netherlands*
[*] *A.Urakawa@tudelft.nl*

Introduction Direct electroreduction of nitric oxide offers a promising avenue to produce valuable chemicals, such as ammonia, which is regarded as an essential building block for fertilizer production.[1] Direct NO conversion to ammonia in a proton exchange membrane (PEM) is advantageous compared to H cells mainly because: a) it overcomes the limitation of low NO solubility in water, and b) it can be operated in a continuous manner.[2] However, at a high current density, the NO reduction reaction is limited by the competing hydrogen evolution reaction (HER). Herein, we report a CO-mediated selective poisoning strategy to enhance the Faradaic efficiency (FE) towards ammonia while suppressing the HER.

Experimental/methodology Electrochemical measurements were conducted in a PEM electrolyzer with a geometric catalyst-coated area of 4 cm^2 and a Nafion 115 membrane. At the anode chamber, IrO_2 was used as the catalyst with 2 mg/cm^2 loading and MilliQ water was supplied. Five different cathode catalysts (Cu/C, Ru/C, Pt/C, Pd/C, and Ag/C with 40 wt.% metal loading on carbon black) were investigated. 2.5% NO or 2.5% NO and CO were supplied continuously at the cathode side.

Results and discussion As depicted in Figure 1, the FE is strongly dependent on the metal and the applied cell potentials during NO electroreduction. In the presence of only NO, Pt/C and Pd/C showed a lower FE towards NH_3 compared to H_2 due to the dominating HER. Cu/C showed 78% FE towards NH_3 at -2.0 V due to the stronger binding affinity to NO* compared to H* (**Figure 1a**). With the co-feeding of CO, the FE of Cu/C towards NH_3 was improved by 12%. More strikingly, for Pd/C, FE towards NH_3 improved by 95% (**Figure 1d**). Moreover, the current density of all the catalysts and FE towards H_2 decreased, while FE towards NH_3 was improved (**Figure 1b and 1e**). This behaviour can be attributed to the change of the microenvironment on the catalyst surface resulting from the selective and competitive binding of CO* to H* binding sites (**Figure 1c and 1f**). As a consequence, the NO* coverage increased on the surface compared to H* coverage, resulting in an improved FE towards NH_3 while suppressing the HER.

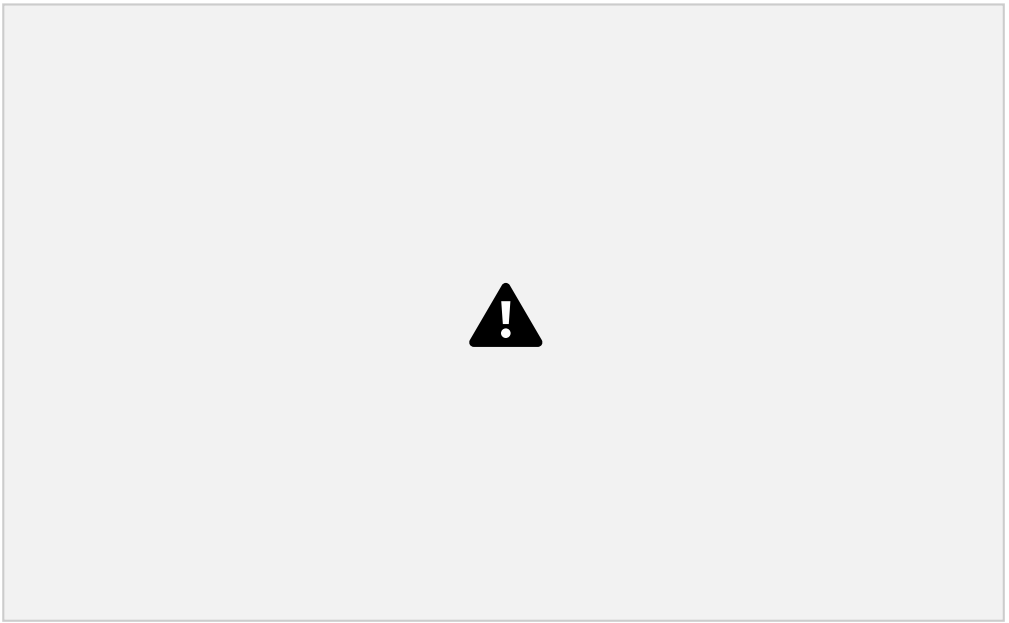

Figure 1. Faradaic efficiency at -1.9 V, -2.0 V, and -2.1 V of various catalysts in (a) NO electroreduction, and (d) NO electroreduction + CO. Total current density vs cell voltage of various catalysts in (b) NO electroreduction, and (e) NO electroreduction + CO. Schematics of (c) NO electroreduction and (f) NO electroreduction + CO on Pd.

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Function-coordinated Electrocatalysts for Carbon Dioxide Reduction

Yuhang Li*, Chunzhong Li

East China University of Science and Technology, Shanghai, China
**yuhangli@ecust.edu.cn*

Keywords: Electrocatalyst, Function coordination structure, Carbon dioxide reduction, Value-added chemicals

Abstract: The electrochemical reduction of carbon dioxide enables the storage of intermittent renewable energy in the form of chemical bonds. Further progress is required in the electrocatalysts which facilitate the conversion chemistry. The functional coordination structures of the electrocatalysts have been regarded as important factors for the catalytic performance of carbon dioixde reduction. By using the oxygen-containing functional groups of water-soluble polymers, we have regulated the reaction microenvironment for catalyst synthesis, and created the cluster-sized catalysts with rich oxygen donors [1-3]. We found out that this kind of metal oxide catalysts exhibited excellent activity and selectivity for carbon dioxide reduction. Further, we have proposed a strategy to improve catalyst stability for carbon dioxide reduction, that is, by enhancing the oxygen transfer processes in the micro-region of electrode/electrolyte interface. By optimizing the electrolyte formula to match the catalytic materials, the applicant promoted the stability of the oxygen-containing active sites in metal oxide catalysts, thus achieving a cathode energy efficiency of more than 75% at high current density for carbon dioxide reduction [4-6]. Recently, we have proposed to couple the processes of cathode and anode reactions, and devised a redox-mediated electrocatalytic reactor. This reactor realized the efficient production of ethylene oxide from carbon dioxide with low energy input and high conversion rate [7].

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The name of presenting author should be underlined.

Fluorine-doped lanthanum strontium cobalt ferrite perovskites as cathodic materials: investigation of ORR and CO_2RR

F. Deganello[1], C. Aliotta[1], R. Thangavel[1], V. La Parola[1], E. La Greca[1], L.F. Liotta[1]

[1] *Institute for the Study of Nanostructured Materials, National Coucil Research (ISMN-CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy*
[*] *leonardafrancesca.liotta@cnr.it*

Keywords: Solution Combustion Synthesis, Fluorine-doped lanthanum strontium cobalt ferrite, electrochemical CO_2 reduction

Introduction. The tremendous usage of fossil fuels and the subsequent CO_2 emission pose environmental pollution. The electrochemical reduction of CO_2 (CO_2RR) is an effective strategy to concurrently reduce CO_2 emissions and manufacture of chemicals and fuels. However, CO_2RR is difficult due to the inherent stability of the C=O bond, particularly at low temperatures [1]. Thus, the development of catalysts with excellent mixed ionic and electronic conductivity, redox cycle stability and high durability is necessary.
Perovskite-based oxides have been indicated among the best performing materials, due to their high conductivity and structural stability [2]. In recent years, fluorine-doped perovskites, where O is partially replaced by F, attracted much attention owing to their high of CO_2 adsorption capacity and surface oxygen vacancies concentration [3]. This study deals with the investigation of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ (LSCF) perovskites doped with two different molar concentration of F, added to increase the oxygen vacancies and, thus, the electrochemical reduction activity. Two preparation strategies, Solution Combustion Synthesis (SCS) and citrate method have been used.

Experimental/methodology. Two F doped-LSCF perovskites, with composition, $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{2.9}F_{0.1}$ and $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{2.8}F_{0.2}$, and the undoped $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ reference compound, were prepared by SCS and citrate method. In both methodologies metal nitrates were used as metals precursors, while NH_4F was used as fluorine source. The final materials were calcined at 900 °C for 4 hours at ramp rate of 10 °C/min. All samples were characterized by X-ray diffraction (XRD) and Rietveld refinement, N_2 physisorption, H_2-temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS). The electrocatalytic activity was investigated by electrochemical impedance spectroscopy (EIS) after deposition on a $Ce_{0.8}Sm_{0.2}O_{2-x}$ (SDC) electrolyte. The EIS spectra were collected from LSCF/SDC/LSCF symmetrical cells between 500 and 900 °C employing Methrohm Autolab impedance analyzer (AC voltage of 0.3 V) equipped with a ProboStat from NorECs.

Results and discussion. XRD characterization evidenced an increased cell volume and larger microstrain of the perovskite structure as function of the fluorine molar concentration, suggesting insertion of the dopant into the lattice. Preliminary ORR analyses were carried out in air. The improved performance of the F doped material, in terms of surface exchange and oxygen bulk diffusion, was confirmed for the

$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{2.9}F_{0.1}$ achieving area specific resistance (ASR) values as low as 0.1 Ω cm^2 at 805 °C, and 0.4

Ω cm^2 at 705 °C.

Acknowledgments
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Nickel decorated carbon nanotubes (CNTs) derived from bioethanol as electrocatalysts for featuring H_2 production and biorefinery

W. Nunthakitgoson. A. Sohail, S. Tiwtusthda, P. Chaipornchalen, A. Thivasasith, and C. Wattanakit*
Department of Chemical and Biomolecular Engineering, School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong, 21210, Thailand
**Corresponding author: chularat.w@vistec.ac.th*

Introduction. The development of the new technology for biorefinery and hydrogen production is one of the most interesting topics for both academic and industrial points of view. Herein, we demonstrate the concept of electrocatalyst development for the simultaneous biomass-derived compound upgrading and hydrogen production via electrochemical approaches. The highly efficient electrocatalysts for both anodic and cathodic parts have been extensively designed for maximizing the catalytic performance with low energy consumption. It is well-known that the Ni-based catalysts have been reported as highly efficient heterogeneous catalysts for electrochemical oxidation of 5-hydroxymethylfurfural (5-HMF). [1,2] However, Ni alone lacks catalytic stability. Indeed, various carbon materials have been coupled with Ni to improve its catalytic performances due to the synergistic effect of carbon and Ni to improve conductivity and electronic structure of active sites. This contribution describes the fabrication of nickel decorated carbon nanotubes (NiCNTs) via chemical vapor deposition (CVD) methods from bioethylene *via* dehydration of bioethanol as a carbon source. [3,4] The fabricated NiCNT electrodes act as bifunctional electrocatalysts on both anode and cathode sides for efficient HMF oxidation coupled with hydrogen generation.

Experimental/methodology. To fabricate working electrodes, the nickel-CNT composite powder was dispersed onto compressed nickel foam (NiCNTs/NF). The electrochemical properties of NiNCTs/NF were investigated with an autolab/PGSTAT 10 potentiostat using a two-electrode setup, NiCNTs/NF as working electrodes for both cathodic and anodic sides. The anodic compartment consisted of a certain amount of HMF in 1 M potassium hydroxide (1M KOH), while the cathodic compartment contained 1 M KOH. To start the catalytic study, a certain amount of HMF was dissolved in the solution. The reaction mixtures for both HMF oxidation and hydrogen production were analyzed using high-performance liquid chromatography (HPLC) equipped with PDA detector and C-18 column. The amount of hydrogen (H_2) production and its Faraday efficiency were measured by gas chromatography (GC).

Results and discussion. Figure 1 shows the kinetic curves of HMF electrooxidation over NiCNTs at a constant potential of 1.45 V vs NiCNTs/NF . For the mechanistic point of view, HMF oxidation can be taken place via HMFCA as an intermediate, which can further transfer to FFCA. After 2 hours of the reaction time, a dramatic increase in FDCA selectivity to 95 %, and 100 % HMF conversion was obtained . Interestingly, the cathodic part initially produced hydrogen at a modest rate of 33 µmol mg^{-1} h^{-1} . Furthermore, the hydrogen generation rate was significantly increased to 75 µmol mg^{-1} h^{-1} when the reaction time is extended to 2 hours, as illustrated in Figure 1B. This strategy can illustrate the rational design of highly efficient electrocatalyst for valorizing the biomass-derived compounds to high-value-added chemicals through electrochemical process.

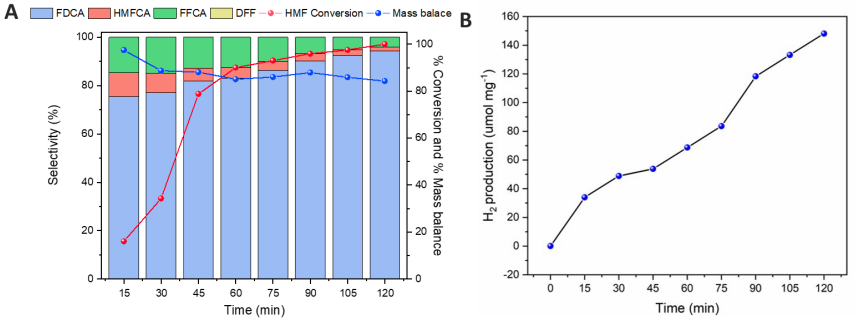

Figure 1 Kinetic Study of NiCNTs/NF at 1.45 V (vs. NiCNTs/NF) A) for electrooxidation of HMF and B) HER in 1 M KOH.

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High Durability of Brownmillerite-type $Ca_2Fe_{0.75}Co_{1.25}O_5$ as Oxygen Evolution Catalyst in Neutral pH Range

H. Okada[1], E. Tsuji[1*], S. Kitano[2], H. Habazaki[2], S. Suganuma[1] and N. Katada[1]

[1]*Center for Research on Green Sustainable Chemistry, Tottori University, Tottori, Japan*
[2] *Faculty of Engineering, Hokkaido University, Sapporo, Japan*
[*]*e-tsuji@tottori-u.ac.jp*

Introduction. Oxygen evolution reaction (OER) is the counter reaction of valuable reduction-type reaction such as CO_2 electroreduction in aqueous solutions. OER is one of the bottlenecks for overall reactions because it requires high overpotential. Many candidate materials were proposed for OER catalysts under alkaline conditions, because the OER readily progresses at high pH. However, most OER catalysts lose the activity due to the surface amorphization and cation leaching under neutral conditions, although the neutral conditions are necessary for CO_2 reduction.[1] Brownmillerite (BM) -type Sr_2GaCoO_5, which was categorized oxygen-deficiency-ordered perovskite (PV) -type oxide, was reported to maintain its activity for a long time under neutral conditions. [1] In this study, BM-type Ca_2FeCoO_5 which is highly active in alkaline conditions[2] was synthesized with different Co/Fe ratios, and its activity and durability were investigated by electrochemical measurements in neutral conditions.[3]

Experimental/methodology. Oxides precursors were synthesized by the sol-gel method[3] using nitrates of Ca, Fe and Co, and citric acid (molar ratio = 2 : 2−x : x : 4, 0 ≤ x ≤ 1.25). The precursors were calcined at 1073 K for 6 h to obtain CFCO-x. Chronopotentiometry at 4.7 mA cm^{-2} were performed using a three-electrode system. The oxide powders, acid-treated acetylene carbon black and neutralized 5 % Nafion® solution were dispersed into ethanol. The thus formed ink was dropped on a carbon paper to prepare a working electrode with the catalyst loading 0.2 mg cm^{-2}. A Pt foil and Ag/AgCl/KCl (satd.) were used as counter and reference electrodes, respectively. An electrolyte containing 0.4 M NaH_2PO_4, 0.6 M Na_2SO_4 and NaOH (pH 7) after N_2 bubbling was employed. Crystal phase of CFCO-1 and -1.25, before and after durability test for 24 h was analyzed by HR-TEM.

Results and discussion. Fig. 1a shows time courses of overpotential against OER at 4.7 mA cm^{-2} at pH = 7. The overpotential of BM-type CFCO-1 in the initial period was lower than those of PV-type $LaFe_{0.5}Co_{0.5}O_3$ and $SrFe_{0.5}Co_{0.5}O_3$, suggesting that BM-type CFCO-1 possessed higher activity for OER in the neutral solution compared to PV-type oxides. The increase in overpotential was slow for CFCO-1, whereas that was apparent on PV-type oxides within a few hours. Furthermore, the overpotential in CFCO-1.25 increased little over 80 h. Fig. 1b-e shows HR−TEM images of (b), (c) CFCO-1.25 and (d), (e) CFCO-1; (b) (d) are before, and (c) (e) are after chronopotentiometry for 24 h. Lattice fringes attributed to BM-type structure were observed on the surface of CFCO-1.25 and CFCO-1 before OER reactions. After OER reactions for 24 h, many BM-type nanocrystals were dispersed in an amorphous matrix near the surface of CFCO-1.25, whereas the BM phase was not observed in CFCO-1. These results suggest that the maintenance of BM phase contributed to the durability of CFCO-1.25, and this is supported by the reported stability of Sr_2GaCoO_5 with BM structure. [1] Thus, the BM-type structure played key roles for the OER in neutral pH range, as well as the Co content itself affects the nature of catalyst.

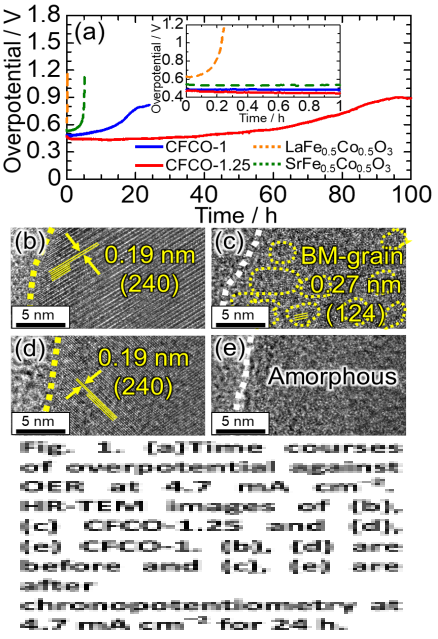

Fig. 1. [a]Time courses of overpotential against OER at 4.7 mA cm^{-2}. HR-TEM images of [b], [c] CFCO-1.25 and [d], [e] CFCO-1. [b], [d] are before and [c], [e] are after chronopotentiometry at 4.7 mA cm^{-2} for 24 h.

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Tailored Nanoparticles as Outstanding Bifunctional Electrocatalysts for pH Universal Water Splitting

J. Martínez,[1] C. Galdeano,[1] I. Márquez,[2] J. Mazarío,[1] J. J. Calvente,[2] J. L. Olloqui,[2] P. Oña-Burgos[1*]

[1] Instituto de Tecnología Química, Universitat Politècnica de València Consejo Superior de Investigaciones Científicas (UPV-CSIC), Avda. de los Naranjos s/n, 46022 Valencia, Spain.

[2] Departamento de Química Física. Universidad de Sevilla. Profesor García González 1, 41012 Sevilla. Spain.

**pasuabur@itq.upv.es*

Keywords: MOF, Nanoparticles, Overall Water Splitting, Tailored Multifunctional Electrocatalysts.

Introduction. Water splitting is one of the key processes for many applications related to energy storage and conversion. This process combines two half-cell reactions to produce hydrogen and oxygen gases, namely the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. The benchmark HER electrocatalysts are platinum (Pt)-based materials, but these are not good for OER, whereas iridium and ruthenium oxides are the state-of-art OER electrocatalysts. Unfortunately, they show insufficient activity toward HER.

Results and discussion. Based on that, herein we report a straightforward, efficient and robust synthesis of mono- and bimetallic nanoparticles, promoted through a commercially available metallic source. For instance, the Wilkinson complex in order to prepare Rh_2P nanoparticles, which have high crystallinity and are coated with graphitic carbon patches.[1] The resulting materials have been tested in electrocatalytic HER and OER processes at acid, alkaline and neutral media, providing superb HER activity and competitive OER performance, particularly at neutral and alkaline media, compared to the benchmark HER and OER electrocatalysts Pt and RuO_x/IrO_x, respectively (Figure 1a).[2]

Besides, supported Fe-doped Pd-nanoparticles (NPs) have been prepared via soft transformation of a PdFe-MOF.[3] The thus synthesized bimetallic PdFe NPs are supported on FeOx@C layers, which are essential for developing well-defined and distributed small NPs. The application of this material (PdFe@FeOx-C) as a multifunctional nanocatalyst for the electrocatalytic water splitting process has been investigated with promising results, compared with those obtained for previously mentioned benchmarking catalysts, in terms of favorable intrinsic activity, wide pH window and high stability (Figure 1b).[4]

Figure 1. HER for Rh_2P@Carbon@Nafion catalysts.

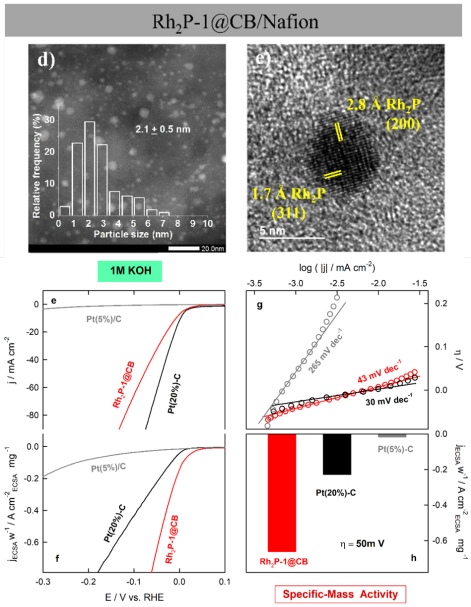
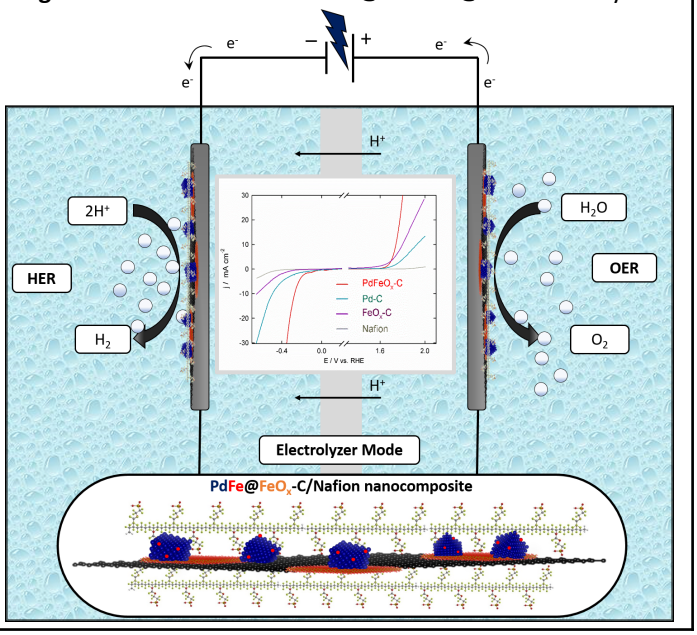


Figure 2. HER and OER for PdFe@FeOx-C@Nafion catalysts.



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Electrocatalytic performance of the composites containing N-doped carbon nanotubes and iron nanoparticles in oxygen reduction reaction

A. Paculą[1*], J. Gurgul[1], R. P. Socha[1], M. Ruggiero-Mikołajczyk[1], B. D. Napruszewska[1], P. Pietrzyk[2], D. Duraczyńska[1], G. Mordarski[1]

[1]*Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland*
[2]*Faculty of Chemistry, Jagiellonian University, Krakow, Poland*
[*]*aleksandra.pacula@ikifp.edu.pl*

Keywords: electrochemical oxygen reduction reaction, Fe-containing CNTs doped with nitrogen

Introduction. Deng et al. [1] experimentally and computationally demonstrated that the interaction of Fe nanoparticles (NPs) encapsulated inside carbon nanotubes (CNTs) with the graphitic walls of the CNTs might lead to a decreased local work function on the carbon surface. In addition, doping nitrogen into the carbon lattice might further reduce the local work function. The reduced local work function at the carbon surface with iron sitting below was expected to enhance its ORR activity. A series of the composites containing N-doped carbon materials and Fe NPs embedded in CNTs was synthesized via chemical vapour deposition (CVD) with acetonitrile (as carbon and nitrogen source) at 600 or 700 °C for 30 minutes in the presence of metal oxides derived from layered double hydroxides (LDHs) of various (low (Fe/Al = 0.25) marked as L or high (Fe/Al = 0.67) marked as H) concentrations of iron ions in MgFeAl systems, having constant Mg/(Fe+Al) atomic ratios, equal 3. The samples were treated with hydrochloric acid in order to remove inorganic compounds such as metal/metal oxides, which were not anchored to the carbonaceous component.

Experimental/methodology. The physicochemical features of the obtained composites were described by means of several techniques including powder X-ray diffraction (XRD), elemental analysis (EA), volumetric nitrogen soprtion, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning electron microscopy (SEM) and X-ray fluorescence (XRF) analysis. The performance of the composites for oxygen reduction reaction (ORR) was evaluated in 0.1 M KOH by means of cyclic voltammetry (CV) and linear sweep voltammetry (LSV) in an electrochemical cell in conventional three-electrode configuration using glassy carbon disk covered with the studied sample as a working electrode, Pt wire and $Ag/AgCl/KCl_{sat}$ electrode as counter and reference electrodes, respectively.

Results and discussion. Depending on the composition of LDHs ($Mg_3Fe_{0.2}Al_{0.8}$ or $Mg_3Fe_{0.4}Al_{0.6}$) and/or synthesis temperature, the resulting N-doped carbon materials consisted of plate-like particles and carbon nanotubes of various contributions. As a result the obtained carbon materials had different concentrations of nitrogen, contents of Fe species and specific surface areas. The composites of N-doped carbon materials with Fe NPs were active in the electrochemical reaction of oxygen reduction in alkaline medium. Judging by the value of limiting current, the following order of the ORR selectivity was observed: C-MgFeAl-L-600-30 < C-MgFeAl-H-600-30 < C-MgFeAl-L-700-30 < C-MgFeAl-H-700-30 in line with increasing population of CNTs, decreasing exposure of graphitic edges (I_{D1}/I_G ~ 3.5, 2.7, 2.4, 2.2) and diminishing contribution of amorphous carbon (I_{D3}/I_G ~ 0.85, 0.61, 0.44, 0.35). The number of electrons involved in ORR calculated by Levich equation was equal 2.0, 2.3, 2.4, 2.9. This trend in selectivity might be due to enhanced interaction of Fe NPs and carbonaceous layers, which was especially pronounced in the sample prepared at 700 °C using $Mg_3Fe_{0.4}Al_{0.6}$ LDHs containing the highest population of Fe species, i.e. 4.1 wt. % (determined by XRF). To verify the impact of Fe content in LDHs on the ORR performance of the composites, additional sample was prepared at 700 °C using MgFeAl LDHs with very high Fe content (Fe/Al = 1) marked as VH. The limiting current and number of electrons were comparable for C-MgFeAl-VH-700-30 and C-MgFeAl-H-700-30.

Acknowledgments
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The composites of N-doped carbon materials and iron species – synthesis, characterization and evaluation in oxygen reduction reaction

A. Paculą[1*], J. Gurgul[1], M. Ruggiero-Mikołajczyk[1], P. Pietrzyk[2], D. Duraczyńska[1]

[1]*Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland*
[2]*Faculty of Chemistry, Jagiellonian University, Krakow, Poland*
[*]*aleksandra.pacula@ikifp.edu.pl*

Keywords: electrochemical oxygen reduction reaction, carbon materials doped with nitrogen

Introduction. Defects in graphitic lattice, both structural and induced by dopants (for example nitrogen in N-doped carbon materials), are beneficial as they result in (a) increasing specific surface area, (b) creating catalytic sites, (c) creating anchoring sites for active species to construct composites. Defective sites in the carbon framework play an important role in electrocatalysis as defects are often active sites [1-3]. A series of the composites containing N-doped carbon materials and iron nanoparticles (NPs) embedded in carbon nanotubes was synthesized via chemical vapour deposition (CVD) with acetonitrile (as carbon and nitrogen source) at 600 or 700 °C for 180 minutes in the presence of metal oxides derived from layered double hydroxides (LDHs) of various (low (Fe/Al = 0.25) marked as L or high (Fe/Al = 0.67) marked as H) concentrations of iron ions in Mg-Fe-Al systems, having constant Mg/(Fe+Al) atomic ratios, equal 3. The samples were treated with hydrochloric acid in order to remove inorganic compounds such as metal/metal oxides, which were not anchored to the carbonaceous component.

Experimental/methodology. The physicochemical features of the obtained composites were described by means of several techniques including powder X-ray diffraction (XRD), elemental analysis (EA), volumetric nitrogen soprtion, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and scanning electron microscopy (SEM). The performance of the composites for oxygen reduction reaction (ORR) was evaluated in 0.1 M KOH by means of linear sweep voltammetry in an electrochemical cell in conventional three-electrode configuration using glassy carbon disk covered with the studied sample as a working electrode, Pt wire and Ag/AgCl/KCl_{sat} electrode as counter and reference electrodes, respectively.

Results and discussion. Depending on the composition of LDHs ($Mg_3Fe_{0.2}Al_{0.8}$ or $Mg_3Fe_{0.4}Al_{0.6}$) and/or synthesis temperature, the resulting N-doped carbon materials consisted of plate-like particles and carbon nanotubes of various contributions. As a consequence the obtained carbon materials had different concentrations of nitrogen, populations of functional N-containing groups, contents of Fe species, specific surface areas and pore diameters. The carbon materials differed not only in the total pore volume and the contribution of micropores and mesopores but also in geometry of mesopores. The composites of N-doped carbon materials with Fe NPs were active in the electrochemical reaction of oxygen reduction in alkaline medium. The number of electrons involved in ORR calculated by Levich equation was equal 2.5, 2.3, 2.4, 2.5. The ORR performance of the samples was roughly comparble. However, more precise analysis of the experimental data revealed essential differences and important correlations. Judging by the value of kinetic current, the following order of the ORR activity was observed: C-MgFeAl-L-600 < C-MgFeAl-H-700 < C-MgFeAl-L-700 < C-MgFeAl-H-600 in line with increasing value of onset potential: - 0.03 V < - 0.02 V < + 0.01 V < + 0.03 V. This trend in activity was consistent with increasing interaction of metal (Fe) NPs encapsulated inside CNTs with graphitic walls of CNTs and growing contribution of pyridinic nitrogen (both supported by XPS) as previousely reported in the literature [4, 5].

Acknowledgments
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Low iridium content mixed-metal oxides for acidic OER in PEM-water electrolysers

T. Prölß[1], T. Franken[1*]

[1] *Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Institute of Chemical Reaction Engineering (CRT), Group of Catalytic and Electrocatalytic Systems and Processes, Erlangen, Germany.*
[*] *tanja.franken@fau.de*

Keywords: water electrolysis, catalysis, electrocatalysis, OER, rotating-disc-electrode

Introduction. The production of green hydrogen via PEM-water-electrolysis is an important part of the energy transition towards renewable energies. Hereby the rate-determining step, the oxygen evolution reaction (OER), is currently catalysed by IrO_2. Iridium however is very expensive. The high price limits its broad applications. Therefore, electrolysers using pure IrO_2 cannot fulfil the growing demand of green hydrogen. As there is no known stable non-noble-metal catalyst with sufficient activity[1], it is necessary to develop novel OER catalysts that maintain high activity with significantly lower Ir-loading. Our approach is to disperse iridium in an atomic dispersion to gain full accessibility of Ir sites and enhance the activity per mass of iridium.

Experimental/methodology. We achieve this by embedding iridium in mixed-metal-oxides like perovskites or spinels. To obtain the desired composition, the catalysts are synthesized from their respective precursor salts via a modified sol-gel route and calcinated in air. The successful inclusion of different amounts of iridium in the non-noble oxide crystal structure is proven by XRD and ICP measurements. The OER-activity and stability is subsequently determined by half cell experiments with a rotating-disc-electrode (RDE) in acidic electrolyte.

Results and discussion. Through fine-tuning of the perovskite and spinel cation-composition, highly stable and active OER-catalysts can be obtained. By substituting non-noble octahedral cations in the different lattice structures with iridium we receive finely dispersed and distorted IrO_6 octahedrons. Based on XRD measurements we show the variation of unit cell and reflex shift caused by the incorporation of different iridium-amounts in the non-noble mixed-metal oxide precursors. We show the OER activity for the catalysts with different iridium contents (figure 1a). The activity per mass of iridium is strongly dependent on the share of iridium in the oxide (figure 1b). By long time electrocatalytic RDE measurements the stability in dependence of the iridium content is discussed as well. Additionally, the influence of different crystal structures on the iridium activity in acidic OER is discussed. Iridium doped mixed-metal-oxides are a promising new group in acidic OER catalysis. Through interactions between the iridium and their neighbouring non-noble metals it is possible to enhance both, the activity per mass of iridium and the catalyst stability.

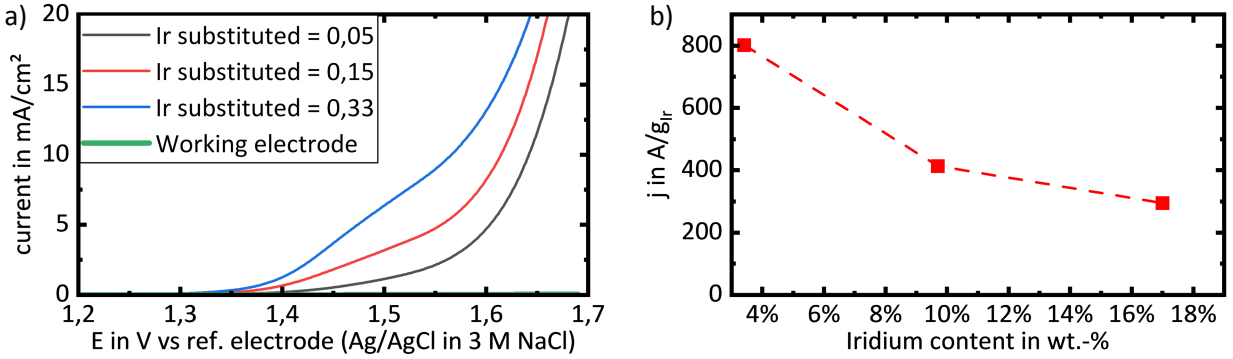

Figure SEQ Figure * ARABIC 1: a) Electrocatalytic activity of synthesized Ir-containing oxides in half cell experiments in 0,5 M H_2SO_4;
b) current at fixed potential normalized by the mass share of iridium.

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Oxygen-Deficient W-CoOOH Nanostructures for High-Performance Electrochemical Nitrate Reduction to Ammonia

S.A. Raheem[1], G. Ballai[1], I. Szenti[2], H. Haspel[2,3], Z. Kónya[1,2*]

[1]*Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary*
[2]*ELKH-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Szeged, Hungary*
[3]*Centre of Excellence for Interdisciplinary Research, University of Szeged, Szeged, Hungary*
[*]konya@chem.u-szeged.hu

Keywords: electrochemical nitrate reduction, ammonia production, cobalt oxyhydroxide, electrocatalysis

Introduction. The electrocatalytic reduction of nitrate (NO_3RR) to ammonia is a promising route for the efficient and sustainable conversion of a hazardous environmental pollutant (NO_3^-) to a valuable chemical feedstock (NH_3) under ambient conditions. To this end, the synthesis of highly active and selective electrocatalysts is essential [1].

Experimental/methodology. Here, we employed a simple solvothermal method to prepare oxygen-deficient W-doped CoOOH nanostructures (Ov-W-CoOOH) and studied the role oxygen vacancies play in NO_3RR on transition metal oxyhydroxides. Linear sweep voltammetry was carried out to evaluate nitrate reduction activity under alkaline conditions in the presence of 0.1 M KNO_3. UV-vis spectrophotometry was employed for product analysis.

Results and discussion. Ov-W-CoOOH nanostructures showed practically 100 % nitrate conversion in NO_3RR with high Faradaic efficiency and substantial stability towards ammonia production. The improved performance of the oxygen-deficient W-CoOOH was attributed to the reduced energy barrier for NO_3^--to-NH_3 by oxygen vacancies. DFT calculations revealed a much lower adsorption energy of $^*NO_3$ on O_V-FeOOH (200) with (−0.02 eV) than that on FeOOH (200), along with a decreased hydrogen adsorption free energy. The latter implies that NO_3RR is more likely to occur than the competing HER, moreover, the byproducts NO and NO_2 are hardly generated due to the high energy barriers of their release [2]. The importance of defects in NO_3RR mechanism on W-CoOOH was experimentally studied by the controlled formation oxygen vacancies, and the resulted improved performance holds promise for the production of ammonia from nitrate-containing wastewater sources.

Acknowledgments
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Understanding the role of Ag in Cu-Ag bimetallic catalysts in electrochemical Fischer-Tropsch synthesis

Floriane A. Rollier, Marta Costa Figueiredo, Emiel J.M. Hensen
Inorganic Materials and Catalysis, Chemical Engineering and Chemistry, Eindhoven University of Technology
P.O. Box 513, 5600 MB Eindhoven, The Netherlands
f.a.rollier@tue.nl

Growing environmental concerns resulting from the combustion of fossil fuels constitute a strong driving force for developing technologies to produce sustainable chemicals and fuels. Electrochemical reduction of CO (CORR) or CO_2 (CO2RR) to chemicals such as C_1 (methane, methanol) and C_{2+} products (ethylene, propylene, ethanol, propanol, etc.) using green electricity can contribute to this energy transition[1]. CO as a constituent of several waste streams such as steel manufacturing flue gas is a particularly interesting reactant. As the exhaust of blast furnaces is considered an irreducible source of CO_x, converting such carbon-based waste into chemical building blocks helps reducing greenhouse gas emissions. Moreover, sustainable CO can also be obtained by a recently commercialized technology that electrochemically reduces CO_2 to CO[2]. CO is also known to be a key intermediate in the formation of C_{2+} products in CO_2RR[3]. Alternative to conventional CO hydrogenation (Fischer-Tropsch synthesis), we considered here an electrochemical variant to obtain products with C-C bonds. As such, electrochemical conversion of CO to light hydrocarbons and oxygenates can reduce our dependence on fossil resources.

It has been reported that the selectivity and activity towards C_{2+} products can be increased by alloying prevalent Cu catalysts with Ag for CO_2 electroreduction[3,4]. CO spill-over, surface strain and electronic effects have been proposed to explain the positive effect of Ag[5,6]. However, the precise role of Ag along with the Cu-Ag interactions in these bimetallic systems remain under debate, especially for the case where CO is electrochemically reduced. As CORR constitutes a pivotal step in C-C coupling processes, we investigated the role of Ag in Cu-Ag electrocatalysts in the production of C_{2+} products from CO. Sol-gel synthesis was used to obtain nanoparticle catalysts with varying Cu-Ag composition. Chronoamperometry revealed that the presence of Ag impacts the catalytic performance with optimum C_{2+} selectivity obtained at a Cu:Ag ratio of 90:10 (Fig. 1). To understand the interactions between Cu and Ag under reaction conditions, we studied the catalysts using operando X-ray absorption (XAS) and quasi in situ X-ray photoelectron spectroscopy (XPS) with the goal of defining structure-activity relationships in CORR to C_{2+} products. The formation of a Cu-Ag alloy was excluded by bulk sensitive characterization techniques such as XAS. However, the XPS analysis pointed to clear differences in Ag dispersion at the catalyst surface depending on composition, which likely influences the amount of Cu-Ag interface sites. These findings help to explain the differences in catalytic performance as a function of Cu:Ag ratio.

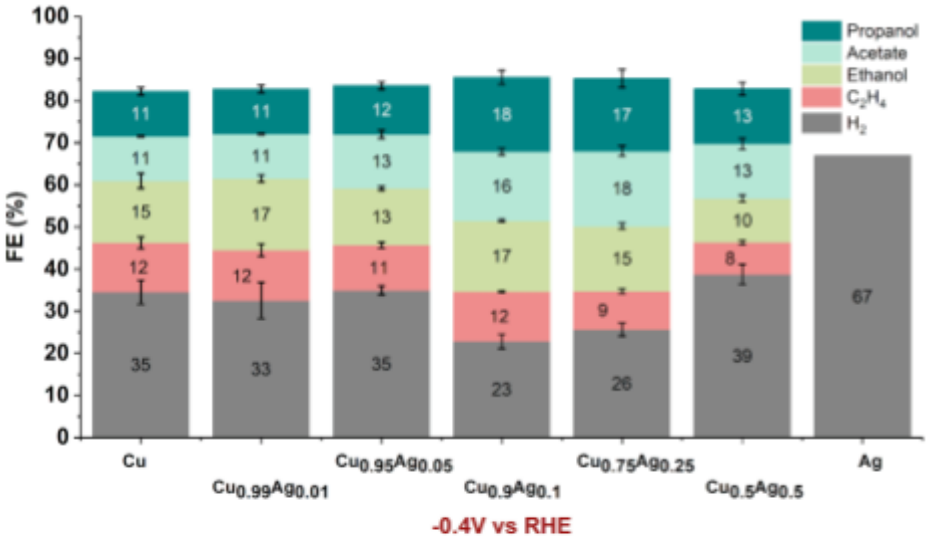

Figure SEQ Figure * ARABIC 1 - Faradaic efficiencies of majored products formed on different Cu-Ag compositions (1h of CORR at -0.4 V vs RHE in 3M KOH)

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Enhancement of Selectivity during Electrocatalytic Reduction of Carbon Dioxide at Copper Centers Supported onto Nonstoichiometric Oxides

Iwona A. Rutkowska*, Anna Chmielnicka, Pawel J Kulesza

Faculty of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland
ilinek@chem.uw.edu.pl

Of particular interest to the preparation of advanced catalytic materials is efficient utilization of catalytic sites (metal and metal oxide nanostructures, their stabilization and intentional activation, as well as organization into two-dimensional arrays, ultra-thin films or three-dimensional networks (e.g. through sequential deposition) on electrode surfaces. They can form nanosized materials with well-defined composition, structure and thickness that exhibit desirable electrocatalytic properties (e.g. toward reduction of CO_2). We explore here the ability of polynuclear inorganic metal oxo systems to stabilize and functionalize metal (e.g. copper) nanostructures. Here certain nanostructured metal oxides of zirconium, titanium, zinc or tungsten have been demonstrated to influence supported metal centers in ways other than simple dispersion over electrode area.

Our research interests concern development of systems for the electrocatalytic reduction of carbon dioxide in acid media[1]. A hybrid catalytic system composed of copper(I)-oxide-derived copper-nanocenters immobilized within the network tungsten oxide nanowires has exhibited electrocatalytic activity toward CO_2-reduction in acid medium (0.5 mol dm^{-3} H2SO4). The catalytic system facilitates conversion of CO_2 to methanol and is fairly selective with respect to the competing hydrogen evolution. The preparative procedure has involved voltammetric electroreduction of Cu_2O toward formation and immobilization of catalytic Cu sites within the hexagonal structures of WO_3 nanowires which are simultaneously partially-reduced to mixed-valence hydrogen tungsten(VI,V) oxide bronzes, H_xWO_3, coexisting with sub-stoichiometric tungsten(VI,IV) oxides, WO_{3-y}. After the initial loss of Cu through its dissolution to Cu^{2+} during positive potential scanning up to 1 V (vs. RHE), the remaining copper is not electroactive and seems to be trapped within in the network of hexagonal WO_3. Using the ultramicroelectrode-based probe, evidence has also been provided that partially-reduced non-stoichiometric tungsten oxides induce reduction of CO_2 to the CO-type reaction intermediates. The existence of copper sites dispersed in WO3 improves electron transfers and charge propagation within the hybrid catalytic layer. The enhanced tolerance of the catalyst to the competitive hydrogen evolution during CO_2-reduction should be explained in terms of the ability of HxWO3 to consume protons and absorb hydrogen as well as to shift the proton discharge at Cu toward more negative potentials. But the capacity of WO_3 to interact with catalytic copper and to adsorb CO-type reaction intermediates is expected to facilitate removal of the poisoning CO-type adsorbates from Cu sites. On mechanistic grounds, the existence of hydrogen-rich partially-reduced tungsten oxides, H_xWO_3, which contain large population of delocalized electrons and monoatomic H, or coexisting protons and electrons, $H^+ + e^-$, is likely to induce hydrogenation of CO-type adsorbates on Cu to form -CH_2OH intermediates followed by protonation. The hybrid Cu/WO_3 system, while exhibiting better selectivity toward CO_2 reduction, relative to hydrogen evolution (proton discharge), is also characterized by improved durability, relative to pristine Cu_2O-dervided copper.

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Effect of the reductive treatment of composite supported Pt electrocatalysts for PEM fuel cell applications

C. Silva[1,2,*], I. Borbáth[1], A. Tompos[1], Gy. Sáfrán[3], Z. Pászti[1]

[1]*InstitutResearch Centre for Natural Sciences, Eötvös Loránd Research Network (ELKH), Budapest, Hungary*
[2]*Department of Physical Chemistry and Materials Science, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Budapest, Hungary*
[3]*Centre of Energy Research, Eötvös Loránd Research Network (ELKH), Budapest, Hungary*
[*]*Corresponding Author: flakcriss45@gmail.com*

Keywords: Mo-doped mixed oxide composite, Pt, strong metal-support interaction, XPS, electrocatalysis

Introduction. Composites of titania-based mixed oxides and carbon denoted as $Ti_{(1-x)}M_xO_2$-C (M = Mo) have recently been identified as promising novel support for Pt electrocatalysts in polymer electrolyte membrane fuel cells (PEMFCs) [1]. The carbonaceous part of the composite ensures the required high surface area and good electrical conductivity of the catalyst, the TiO_2 component helps to stabilize Pt particles against dissolution and/or sintering driven by electrooxidation of the carbon, while the dopant metal cations incorporated into the titania improve the conductivity and provide valuable co-catalytic function, thus the composite supports can mitigate the known drawbacks of the current state-of-art Pt/C systems. The strong metal-support interaction (SMSI) phenomenon can occur in the composite supported electrocatalyst due to the interaction of Pt and the mixed oxide, generally manifesting itself in decoration of the metal particles by ultrathin layers of the support material upon annealing under reductive conditions [2]. The aim of this work is to evaluate the SMSI phenomenon as a possible strategy for tailoring the properties of the electrocatalysts in terms of stability and activity.

Experimental/methodology. A 20 wt.% Pt/50 wt.% $Ti_{0.8}Mo_{0.2}O_2$-50 wt.% C electrocatalyst prepared on Black Pearls 2000 carbon functionalized with HNO_3 and glucose was reduced at varying temperatures between 150-450 °C in H_2 in order to induce SMSI. Cyclic voltammetry and CO_{ads} stripping voltammetry were used to assess the electrocatalytic properties and the stability of the reduced catalysts compared with the parent one and commercial reference Pt/C catalyst. The hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) were measured by rotating disk electrode (RDE) to evaluate the kinetic behavior of the systems. Structural characterization by XRD and TEM, completed by XPS measurements combined with *in situ* H_2 exposure experiments was performed in order to understand the interaction between the oxide and the Pt nanoparticles [3].

Results and discussion. Electrochemical investigations revealed good activity and tolerance against CO poisoning for both the parent Pt/$Ti_{0.8}Mo_{0.2}O_2$-C catalyst and its reduced counterparts, which was explained by atomic closeness of Pt and easily reducible Mo species as confirmed by TEM. Partial encapsulation of Pt by mobile Mo species was suggested by a slight decrease of the electrochemically active surface area (ECSA) of Pt at reduction temperatures above 150 °C; XPS investigations indeed indicated appearance of ionic Mo directly adsorbed on the Pt surface in this temperature range. Besides, the stability of the reduced catalysts assessed by ECSA changes during a 10,000-cycle stability test significantly improved with respect to not only the commercial Pt/C reference but also to the parent Pt/$Ti_{0.8}Mo_{0.2}O_2$-C catalyst. The systematic variation of the reduction temperature, accompanied by the thorough characterization of the reduced catalysts allowed selection of the most promising treatment conditions and interpretation of the results in terms of structural changes of the catalysts.

Acknowledgments
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Transition Metal Phosphide-Based Materials for HER and OER reactions

N. Spera, J. P. S. Sousa*

International Iberian Nanotechnology Laboratory, Braga, Portugal
*Juliana.Sousa@inl.int

Keywords: phosphides, HER, OER

Introduction. Water electrolysis is a promising technology to produce the high-purity of hydrogen due to its environmental friendliness. However, the best electrocatalysts for this process—which include the hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR)—often contain scarce and expensive noble metals, substantially limiting the potential for these technologies to compete with fossil fuels. The considerable challenge is to develop robust electrocatalysts composed exclusively of low-cost, earth-abundant elements that exhibit activity comparable to that of noble metals [1, 2]. Transition metal phosphides are receiving intense attention due to their abundance in the Earth's crust and comparable catalytic properties to noble metals. The main goal of this project is to explore the properties of transition metal phosphides in order to achieve optimal catalytic performance with sustainable, earth-abundant materials. Active catalysts are required to minimize the overpotential necessary to drive the oxygen (hydrogen) evolution reaction. The doping of phosphides with aluminium (Al) and magnesium (Mg) can have a positive effect on the electrocatalytic activity. The doping will have significant and diverse effects on the electronic structure, the position of the Fermi level, and the curvature of DOS near the Fermi level.

Experimental/methodology. Fe- and Ni-based phosphides with high efficiencies toward electrochemical H_2 and O_2 evolution reactions were prepared. It was performed, a systematic doping of Ni (Co and Fe) P with Al and Mg. The doped phases were characterized to establish bulk crystal structures, the dopant atom distributions, and the resulting bulk electronic structures. The performance of the electrocatalyst was investigated in terms of activity (hydrogen and oxygen production rates) and stability.

Results and discussion. Self-supported electrodes comprising carbon black integrated with transition metal phosphides electrocatalysts were fabricated by one-step phosphorization treatment.

It has been proven that P atoms in the TMPs play crucial roles for HER. The negatively charged P can act as a base to trap positively charged proton during electrochemical HER. So for the same metal phosphides, increasing the atomic percentage of P may effectively improve the corresponding HER activity. However with the continuously doping P into metals, electrically conductive metals gradually become semi-conductive or even insulated metal phosphides. The reason is that P atoms will restrict the electron delocalization in metal, resulting in weakened conductivity, resulting in a weakened electronegativity. Furthermore, in almost all of the phosphides occurred the oxidation of its surface, resulting in the formation of P (V) and metal oxide (high-valence state). This as-formed non-active oxide would clearly block the access of the proton to the active site and lower the conductivity, which will cause fast degradation in performance. So is very important to determine the optimal amount of P to be present in TPMPs.

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Copper/Boron Carbon Nitride Core/Shell Structure for Electrochemical Reduction of Nitrate to Ammonia

A.T.Tabrizi[1], G. Ballai[1], I. Szenti[2], H. Haspel[2,3], Z. Kónya[1,2*]

[1]*Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary*
[2]*ELKH-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Szeged, Hungary*
[3]*Centre of Excellence for Interdisciplinary Research, University of Szeged, Szeged, Hungary*
[*]*konya@chem.u-szeged.hu*

Keywords: electrochemical nitrate reduction, electroless coating, boron carbon nitride (BCN), electrocatalysis

Introduction. Ternary boron carbon nitride (B-C-N or BCN) integrates the merits of the widely-known 2D materials, graphene and hexagonal boron nitride (hBN). BCN materials have drawn attention for their physical and chemical properties, like tunable band structure (band gap between 0 and 5.5 eV by adjusting heteroelement composition) and hence adaptable electrical properties, thermal stability and chemical inertness [1, 2]. This promise diverse possible applications, and since the heteropolar B and N bonding largely stimulates electroactivity, BCN structures are likely to be used in electrochemical energy applications as well. In this study, the performance of a Cu/BCN heterostructure was studied in the electrochemical reduction of nitrate (NO_3RR) towards a valuable chemical feedstock, ammonia.

Experimental/methodology. BCN powder was synthesized through a hybrid method of combining mechanical alloying and calcination. Mechanical alloying was carried out in a planetary ball mill at 450 rpm for 6 h with the subsequent calcination at 500 °C for 2 h under argon atmosphere. Copper layer was deposited onto the as-synthesized compound using electroless plating with and without a prior surface activation using Pd^+ cations, and a core/shell Cu@BCN structure was obtained. NO_3RR activity was evaluated via linear sweep voltammetry under alkaline conditions in the presence of 0.1 M KNO_3, while the corresponding product distribution was determined by UV-vis spectroscopy.

Results and discussion. X-ray diffractometry showed that either Cu_xO or highly crystalline elemental Cu was formed on the pristine BCN during electroless plating with and without Pd^+ surface activation, respectively. The morphology of the obtained heterostructures was studied by scanning and transmission electron microscopy (TEM), and the formation of a non-uniform copper-oxide layer was found in the the former, while a more uniform polycrystalline copper core/shell structure in the latter case. The deposition of copper-based layers then introduced improved activity in electrochemical nitrate reduction, making these structures promising Cu-based electrocatalysts for high-performance ammonia production from nitrate-containing wastewaters [3].

Acknowledgments
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Water electrolysis in molten salts under increased temperatures and pressures

J. Tie[1], F. Bannert[1], E. Christensen[2], N. Bjerrum[2], K. Köhler[1*]

[1]*Technical University of Munich, Garching, Germany*
[2]*Technical University of Denmark, Lyngby, Denmark*
[*]*klaus.koehler@tum.de*

Keywords: Water electrolysis, Hydrogen evolution reaction (HER), Molten salt electrolyte, Electrocatalysis

Introduction.
Excess electrical energy from renewable resources has to be stored in the form of electricity-based energy carriers and fuels, one particular example is hydrogen from electrolysis. Most of the research is carried out in aqueous electrolytes at room temperature (or slightly elevated temperatures) and atmospheric pressure, so-called Low Temperature Electrolysis (LTE). Another interesting approach is to implement proton-conducting salts as electrolytes. This method can be used at higher temperatures, compared to LTE, in ranges between 200 and 400°C and is therefore referred to as Medium Temperature Electrolysis (MTE). The potential for alternative, cost-effective electrode and electrocatalyst materials is very promising, compared to common noble metals (e.g., Platinum) implemented in LTE. We have already successfully carried out corresponding investigations in the MTE range and successfully proven specific carbide materials to be better than platinum under these conditions [1, 2]. The present contribution shows an attractive approach to studying MTE systems including a detailed investigation of different materials.

Experimental/methodology.
A novel electrolyzer construction was developed for elevated pressure and temperature electrocatalytic applications (i.e., MTE) and electrochemical characterization, see figure. This setup is safer and more flexible for the exploration of electrolysis under those elevated temperature and pressure conditions, e.g., water electrolysis in molten salt electrolytes for MTE (this work). Some of the experiments include proton conductivity measurements and eutectic system characterizations of dihydrogen phosphate based salt mixtures (MH_2PO_4, M= Li, Na, K).

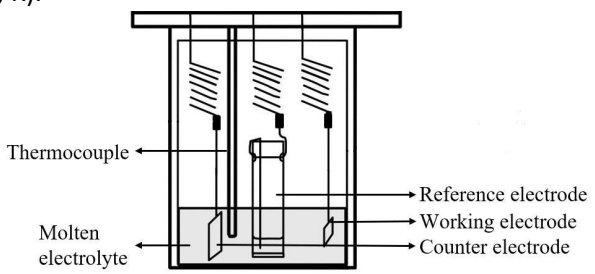

Figure: Setup for electrocatalytic measurements under medium temperature and elevated pressures.

Results and discussion.
The melting and thus the working temperature for the MTE could be adjusted with varying salt mixtures, giving higher process temperature flexibility for electrolysis implementation. Furthermore, a series of electrochemical characterization techniques including Linear Sweep Voltammetry (LSV), Electrochemical Impedance Spectroscopy (EIS), and Chronopotentiometry (CP) were implemented on different transition metal electrodes. The performance of these electrodes shows potential for implementation as low-cost alternative electrocatalyst supports in contrast to Platinum.

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High-entropy Alloys as Oxygen Reduction Reaction Electrocatalysts for Proton Exchange Membrane Fuel Cells Application

Author's Name (Calibri, 12 pt.) e.g. Daniel H. C. Wan[1], Guangyu Chen[2], Jay Hon Chueng Yan[1], Ryan Feng Wang[1*], Minhua Shao[2*]

[1] *University College London, London, WC1E 7JE, UK*
[2] *The Hong Kong University of Science and Technology, Kowloon, Hong Kong SAR, China*

[*] *ryan.wang@ucl.ac.uk; kemshao@ust.hk*

Keywords: Electrocatalysts, Oxygen reduction reaction, High-entropy alloys, Proton exchange membrane fuel cells

Introduction.

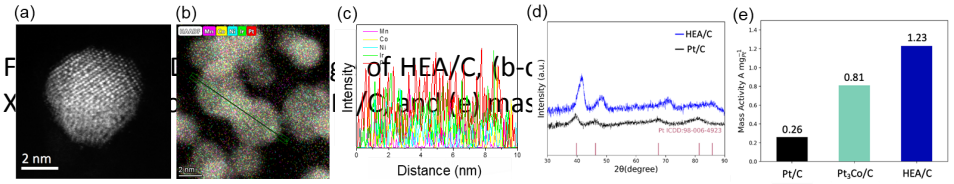
Proton exchange membrane fuel cells (PEMFCs) have been regarded as a promising candidate for fuel cell electric vehicles (FCEVs). Yet, wide application of such technology is greatly dependent on the cost and performance of the oxygen reduction reaction (ORR) catalysts at the cathode. Recently, high-entropy alloys (HEAs) has come out as an emerging class of material for catalysis, and it is appealing for ORR. The multi-metal components could not only reduce the Pt usage but also optimize oxygen adsorption energy by finetuning various alloying composition at an intricate scale compared to conventional binary or ternary alloys, hence attaining high ORR activity.

Experimental/methodology.

The PtCoNiMnIr/C (HEA/C) was synthesized using seed-mediated wet-impregnation method, in which desirable amount of metal precurors were mixed with Pt/C followed by high temperature fast annealing under H_2/Ar. Structure and morphology of the catalyst was studied using various techniques, e.g., XRD, XPS, HAADF STEM, etc.. ORR performance of the catalyst was evaluated using a rotating disk electrode (RDE) setup, from which electrochemical surface areas and mass activities of the catalysts were obtained. In addition, advanced X-ray techniques e.g., XANES, EXAFS and valence to core XES were performed to further elucidate the strucutral-performance relationship of the catalyst.

Results and discussion.

Fig 1a shows the HAADF-STEM image of the HEA/C catalyst, which showed an interesting intermetallic strucuture. The corresponding line scan elemental profile from EDX also indicated an uniform elemental distribution on the HEA nanoparticles. (Fig. 1b-c) XRD pattern of the HEA/C showed a positive peak shift towards higher angle compared to that of Pt/C, which inferred a Pt lattice compression due to alloying. (Fig. 1d) Such lattice strain effect could lower the *d*-band centre of the Pt and weaken the adsorption of oxide species, hence improving the ORR activity. In terms of the ORR performance, the mass activity of the as-prepared HEA/C was found to be 1.23 A/mgPt (Fig. 1e), which was around 1.5 times higher than that of Pt_3Co/C (0.81 A/mgPt) and 4.9 times higher than that of commercial Pt/C catalyst (0.26 A/mgPt). This result has shown that by alloying Pt with multiple metal elements to form HEA, it could achieve superior ORR performance compared to binary Pt alloy and pure Pt. This could primarily due to the incorporation of multiple metal species, which allow precise tuning of the oxygen adsorption energy for more efficient ORR.



F[illegible] of HEA/C, (b-c[illegible] nding line scan profile, (d) X[illegible] /C and (e) mas[illegible] ith Pt_3Co/C and Pt/C.

Investigation of Radical Formation in AEMFCs by Means of *Operando* EPR Spectroscopy

S. Wierzbicki[1,2]*, J.C. Douglin[3], R.K. Singh[3,4], D.R. Dekel[3,5], K. Kruczała[1]

[1]Faculty of Chemistry, [2]Doctoral School of Exact and Natural Sciences, Jagiellonian University in Krakow, Gronostajowa 2, 30-387 Krakow, Poland
[3]The Wolfson Department of Chemical Engineering, Technion-Israel Institute of Technology (IIT),
[5]Grand Technion Energy Program (GTEP), Technion-IIT, Haifa, Israel
[4]CO_2 Research and Green Technologies Centre, VIT Vellore-632014, Tamil Nadu, India
**wierzbicki@chemia.uj.edu.pl*

Introduction. Anion-Exchange Membrane (AEM) Fuel Cells (FCs) are a novel technology, which is a promising alternative to the proton exchange membrane (PEM) FCs, due to the alkaline medium of AEMs which allows the use of electrocatalysts free from Platinum Group Metals (PGM), which contributes to lowering the price of AEMFCs price in comparison to PEMFCs [1,2]. Nevertheless, the low stability of AEMs is still one of the factors hindering wide-scale AEM application. Radical-induced degradation was widely described for PEMs, however, is still not very well understood for AEMs [3]. Radical-based Reactive Oxygen Species (ROS), such as ˙OOH and ˙OH radicals are believed to have crucial on AEMs degradation processes [3-5].

Experimental/methodology. Electron Paramagnetic Resonance (EPR) spectroscopy was used as a primary technique in conjunction with spin trapping, as it allows the detection of short-living radicals formed during AEMFC operation. A micro-AEMFC employing Fumasep FAA-3-20 membrane and one of five cathode catalysts (Pt, Pd, low-PGM PdAg PGM-free $(MnCo)_3O_4$ and Ag) was fitted in an EPR spectrometer cavity, with DMPO spin trap placed on the investigated electrode.

Figure 1. EPR spectra recorded on cathodes of AEMFCs using $(MnCo)_3O_4$ **(A)** and PdAg **(B)** catalysts.

Results and discussion. The formation of ROS was confirmed on all of the investigated cathode catalysts. EPR spectra recorded on cathodes of AEMFCs using $(MnCo)_3O_4$ and PdAg catalysts are showcased in **Figure 1**. Both spectra exhibit hyperfine splittings characteristic for DMPO-OOH adducts. Additional experiments, conducted with $(MnCo)_3O_4$ catalyst exposed to isotope marked $^{17}O_2$, confirmed that the ˙OOH radicals are formed in the interaction of gaseous oxygen with the catalyst surface. The spectrum recorded on the PdAg (**Figure 1B**) catalyst exhibits additional peaks, indicated with the arrows, attributed to the DMPO-H adducts with hydrogen radicals formed due to H_2 diffusion through the membrane. The formation of ˙H and ˙OOH radicals at the cathode during the AEMFC operation is crucial for the understanding of AEM degradation. These findings suggest that it is necessary to develop catalysts containing radical scavenging additives and novel AEMs resistant to radical attack. Thus, in our future studies, we plan to investigate the efficacy of radical scavengers and the effect of the operating conditions on the radical formation in AEMFC.

Acknowledgments
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Direct Ammonia fueled Solid Oxide Fuel Cells: State-of-the-art, catalyst development, and future challenges

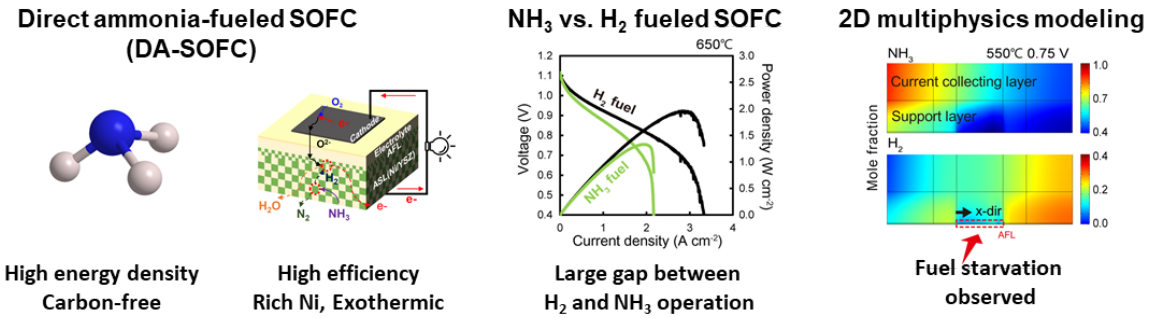
Sungeun Yang[1,2*], Seongkook Oh[1,2], Hayoung Kim[1,3], Min Jun Oh[1,4], Jong-Ho Lee[1,2], Ji-Won Son[1,3]
[1]*Korea Institute of Science and Technology (KIST), Seoul, Republic of Korea*
[2]*Korea University of Science and Technology (UST) KIST School, Seoul, Republic of Korea*
[3]*Korea University, Seoul, Republic of Korea*
[4]*Yonsei University, Seoul, Republic of Korea*
[*]*syang@kist.re.kr*

Keywords: Ammonia, solid oxide fuel cell, direct ammonia solid oxide fuel cell, ammonia decomposition

Introduction. Transitioning into a sustainable energy system is a significant challenge in countries like South Korea; a densely populated country with energy-intensive industries with low potential for renewable energy. Green ammonia is a plausible solution to this problem where ammonia has one of the highest energy densities with well-established infrastructure. Direct ammonia-fueled solid oxide fuel cell (DA-SOFC) is a type of SOFC directly fed with ammonia fuel. Ammonia decomposes into hydrogen and nitrogen inside the Ni-rich anode of SOFC, and hydrogen is electrochemically oxidized to generate electricity with high efficiency. The exothermic operation of the fuel cell and the endothermic reaction of ammonia decomposition increases the efficiency even further making DA-SOFC one of the most attractive devices that use ammonia. DA-SOFCs perform as well as their H_2-fueled counterparts at temperatures > 750 °C but a significant performance drop is observed for the next generation SOFCs that run at < 650 °C.

Experimental/methodology. In this work, state-of-the-art thin-film SOFCs were tested for direct ammonia operation and were compared with a commercial SOFC. Thin-film SOFCs were fabricated by using the pulsed laser deposition method [1]. Electrochemical measurements, impedance spectroscopy, gas analysis, and 2D multiphysics modeling were performed to gain a comprehensive understanding of DA-SOFCs. Further, we focused on the development of high-performance DA-SOFCs through the introduction of thermally stable nano-sized ammonia decomposition catalysts.

Results and discussion. The electrochemical performance test and impedance spectroscopy results were compared between the ammonia and hydrogen operations on three different SOFCs. The performance of DA-SOFC dropped significantly with decreasing temperature and increasing cell performance. The lack of fuel at the electrochemical interface was expected from the impedance analysis. Total ammonia conversion at the cell outlet decreased from 80% to 20% as temperatures were lowered from 650 to 500 °C. Ammonia conversion and electrochemical reactions inside the cells were observed by developing a two-dimensional (2D) multi-physics numerical model. The model suggested that the lower ammonia conversion and mass transport limitations result in the low flux of the hydrogen fuel to the electrochemical interface. The results signified the importance of a better ammonia decomposition catalyst and facile gas transport channels. To further improve the performance of DA-SOFCs, thermally stable and active Ru catalysts were developed and introduced to the SOFCs. The cell showed improved ammonia conversion and DA-SOFC performance. We are also focusing on the detection of potential NO_X emission, degradation of metallic components, and catalytic activity of metallic components of the SOFCs.



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Design of a perovskite oxide cathode for a proton-conducting solid oxide fuel cell

Penghui Yao, Yongdan Li*

Department of Chemical and Metallurgical Engineering, Aalto University, Kemistintie 1, FI-00076 Aalto, Finland

Keywords: Proton-conductive fuel cell (PCFC), Cathode $La_{0.5}Sr_{0.5}Mn_{0.9}Ni_{0.1}O_{3-\delta}$, Oxygen reduction reaction (ORR), Proton transfer.

Introduction. Effective technologies for clean and sustainable energy transformation are highly demanded for addressing the growing energy consumption and environmental pollution. The solid oxide fuel cell (SOFC) have drawn great attention as an efficient, clean, and sustainable energy conversion device[1]. However, high operation temperature (700-1000 °C) has limited their widespread application. In contrast, proton-conductive fuel cells (PCFCs) operate at lower temperatures (550-700 °C) than the conventional oxygen ion-conducting SOFCs. No fuel dilution needed is an additional merit for PCFCs due to the water formation on the cathode side. Nevertheless, sluggish cathode reaction kinetics at low temperatures has been a major challenge for their practical application[2]. High polarization and low electrocatalytic activity toward oxygen reduction reaction (ORR) deteriorate the cell performance. In this work, Ni doped $La_{0.5}Sr_{0.5}MnO_{3-\delta}$ is designed based on DFT simulation and synthesized as cathode material of a PCFC. The effects of the Ni-doping on the crystal structure, electronic configuration and oxygen vacancy formation. Moreover, the proton transfer and ORR mechanism are discussed.

Experimental/methodology. The electrolyte $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) powder was synthesized with a solid-state reaction method[3]. The electrolyte layer was coated on the anode with a dip-coating method. The electrolyte precursor slurry was obtained with ball-milling BZCY, sintering aid NiO, triethanolamine, polyethylene glycol 600, dibutyl phthalate and ethanol. After coating the electrolyte slurry on the anode surface, the anode-electrolyte bilayer was co-sintered at 1400 °C for 5 h. $La_{0.5}Sr_{0.5}MnO_{3-\delta}$ (LSM) and $La_{0.5}Sr_{0.5}Mn_{0.9}Ni_{0.1}O_{3-\delta}$(LSMNi) powders were prepared with a sol-gel technique. Lanthanum nitrate hexahydrate, strontium nitrate, manganese(II) nitrate, and nickel nitrate hexahydrate as the metal sources were dissolved in water. Subsequently, citric acid was added. The molar ratio of citric acid to metal ions was set at 1.5.

Results and discussion. LSMNi as cathode shows higher proton conductivity and ORR activity than the undoped LSM. The PCFCs with LSMNi exhibit low polarization resistance and high peak power density. The density functional theory simulations indicate that Ni doping decreases the oxygen vacancy formation and proton migration energy barriers, thereby improving the proton conductivity. The enhanced ORR activity is attributed to O p-band center close to Fermi level and the overlapping state of 3d orbitals of Mn and 2p orbitals of O, accelerating electron transfer during ORR steps. The adsorption energy of oxygen on the LSMNi surface is lower than that on LSM. This work provides a novel strategy to design cobalt-free cathode for a proton-conductive fuel cell.

Acknowledgments

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Electrocatalytic Hydrogenation of Olefinic and Carbonyl Compounds with Pd@Carbon Nanotubes at an Oil-Water Interface

Chenhui Han[1], Johannes Zenner[1,2], Jacob Johny[1], Nicolas Kaeffer[1], Alexis Bordet[1]*, Walter Leitner[1,2]

[1]*Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany*
[2]*Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany*
[*]*alexis.bordet@cec.mpg.de*

Introduction. Electrocatalytic hydrogenation (ECH) represents an attractive method to use electricity from renewable sources towards the electrification of the chemical sector, from biomass conversion to the production of fine chemicals. Protons from water are reduced electrochemically and directly transferred to unsaturated substrates under mild operating conditions (temperature and pressure), while avoiding the need for H_2 handling and storage.[1] However, in aqueous media this technique is limited by the low solubility of most organic substrates and the competing hydrogen evolution reaction. Organic electrolytes can improve substrate solubility, however their use is typically associated with significant ohmic losses.[2]

Experimental/methodology. To tackle these limitations, a Pickering emulsion-based ECH system was developed. Pickering emulsions consist of two immiscible phases, with one phase being dispersed into the other as micrometer-sized droplets. These droplets are stabilized by solid particles at their interface.[3] In the present work, organic substrates were dissolved in oil droplets (constituted of cyclohexane as organic solvent) surrounded by an acidic aqueous electrolyte. Pd nanoparticle-decorated carbon nanotubes (Pd@CNTs) were employed both as stabilizers for the Pickering emulsions and electrocatalysts (Figure 1a).

Results and discussion. The described configuration simultaneously benefits from the high ionic conductivity of the aqueous phase and good substrate solubility in the emulsion droplets. Electricity is transported from a silver cathode to the large oil/water interface via the conductive Pd@CNTs, where Pd nanoparticles enable the reduction of protons from the aqueous phase. These hydride species can then hydrogenate the substrates inside the oil droplets. The surface molecular modification of the CNTs proved critical to ensure sufficient contact between the cathode and the network of emulsion bubbles. The emulsion-based ECH system showed high mass specific current density (–148.1 $mA \cdot mg_{Pd}^{-1}$) and faradaic efficiency (95.0%) towards the production ethylbenzene from styrene (Figure 1b).[4] This approach was successfully extended to a variety of alkenes, aldehydes and ketones, and we further plan to explore the applicability of this strategy to an extended array of chemical transformations, such as the conversion of bio-oil and biocrude.

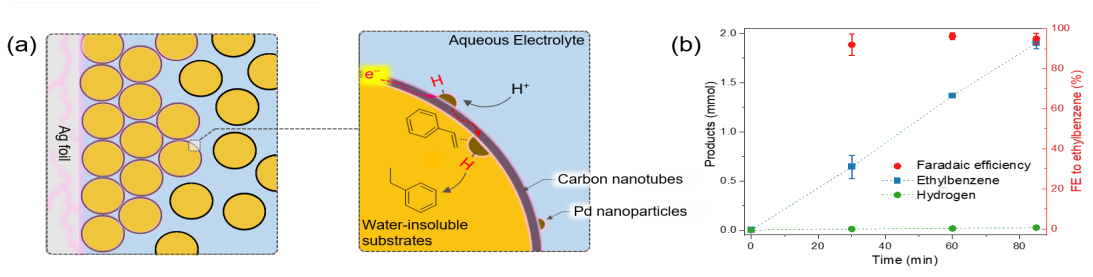

Figure 1. (a) Scheme of the Pickering emulsion based ECH system: Emulsion droplets are stabilized by CNTs, that conduct electricity from a silver electrode to Pd nanoparticles. The NPs catalyze the reduction of protons from water, which then hydrogenate organic substrates in the oil droplets. (b) Time-profile of the ECH of styrene to ethylbenzene using the presented ECH system (0.2 mmol styrene, 10 mg Pd/CNTs (4.7 µmol Pd), 10 mL cyclohexane, 75 mL 0.5 M H_2SO_4, 0.65 V_{RHE}, emulsification frequency 5 s/5 min, reactions were stopped after the passage of 386 C).

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Ru-deposited Cu nanoplate for efficient hydrogen evolution reaction in alkaline water electrolyzers

Y. Zuo[1*], S. Bellani[2], M. Ferri[1], D. Shinde[1], M.I. Zappia[2], R. Brescia[3], M. Prato[4], L.D. Trizio[1], F. Bonaccorso[2,5], L. Manna[1]

[1] *Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*
[2] *BeDimensional S.p.A, Via Lungotorrente Secca, 30R, 16163 Genova, Italy*
[3] *Electron Microscopy Facility, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*
[4] *Materials Characterization Facility, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*
[5] *Graphene Labs, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*
[*] *Corresponding Author's E-mail address: yong.zuo@iit.it*

Keywords: Green hydrogen, Hydrogen evolution reaction, Alkaline water electrolyzer.

Introduction. Electrochemical production of green hydrogen, driven by electricity power derived from renewable energy sources, is a crucial technology to empower the energy transition towards climate neutrality.[1,2] In this scenario, alkaline electrolyzer (AEL) stacks have been robustly established at MW-scale for over a century, with single-stack capacities up to several MWs.[3] However, the energy efficiencies of commercial AELs, particularly at current densities above 0.5 A/cm^2, are still insufficient to make green hydrogen cost-competitive with fossil fuels.[4] In our work, we demonstrate that the main limitations of AELs can be overcome by systematically designing cost-effective cathode and anode with state of the art-like performances for alkaline water splitting reactions and using the recently validated commercial diaphragms for building performance-robust and safe AELs.

Methodology of synthesis. i) Chemical bath deposition of CuO nanoplate arrays onto metallic substrate (*e.g.,* Ti mesh); ii) Electroreduction of CuO nanoplate arrays; iii) Electrodeposition of Ru nanocrystals.

Results and discussion. We designed a cost-effective, highly performant and robust cathode (up to 25 cm^2 working area), consisting of catalytically active electrodeposited Ru nanoparticles (*ca. 53* μgRu/cm^2) on vertically oriented Cu nanoplatelet arrays grown on metallic meshes, namely, Ru@Cu-TM. The mass loading of Ru on cathode is 10 times lower than that of Pt used in proton exchange membrane electrolyzers (PEM-ELs), while achieving a current density of -0.2 A/cm^2 at a low overpotential of 85 mV (>200 mV for Pt/C) in 1M NaOH. Besides, we discovered that multistacked SSMs could be a simple and cost-effective anode to replace the well-performant NiFe anode screened by us for designing AELs, with unprecedented performance and long-term durability. Our optimized AELs, using commercial diaphgrams, can operate with current densities as high as 1 A/cm^2 at 1.69 V and operate at almost 6 A/cm^2 at 2.30 V. The latter reached record values reported for Pt group material-based proton-exchange membrane electrolyzers. Such a AEL could stably operate in a continuous (1 A/cm^2 for over 300 h) and intermittent modes with an estimated total cost of US$2.26/Kg$_{H2}$ for a 1 MW AEL plant based on the proposed electrode technology, hitting the worldwide targets of green hydrogen production for the coming decade (<US$2.5/Kg$_{H2}$).

Acknowledgments
This work has received funding from the European Union's Horizon 2020 "Proof of Concept" programme under Grant Agreement No. 899412 (HyCat) and the European Union's Horizon 2020 research and innovation program under Grant Agreement No. 881603- GrapheneCore3; the European Union's SENSIBAT project under Grant Agreement No. 957273.

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Shape-shifting exsolved nanoparticles in solid oxide cells

Somi Lee, Yo Han Kim, Yeeun Kim and Jae-ha Myung*

Department of Materials Science and Engineering, Incheon National University, Incheon 22012, South Korea
**Corresponding Author's E-mail address: mjaeha@inu.ac.kr*

Introduction. The exsolution method, which allows for the uniform growth and dispersion of nanoparticles on a support oxide, is a promising approach that offers unique stability against carbon coking and agglomeration. Controlling the shape of nano-catalysts improves catalytic properties by adjusting the crystallographic planes involved in the reaction and increasing the surface area.[1,2] However, shape control of nanoparticles in exsolution research has not been extensively studied. To achieve shape-shifting in the exsolution processes, considerable growth of nanoparticles are required to stabilize the surface of metallic particles. In this study, the surface of nanoparticles exsolved from perovskite oxide electrodes was controlled to the (111) plane by maximizing particle growth via electrochemical reduction.
Experimental/methodology. The perovskite oxides were synthesized by solid state reaction method including mixing regents, sintering at 1300 °C for 3 h, and grinding. The synthesized oxides were reduced in pure H_2 at high-temperatures of 600, 750, and 900 °C to achieve exsolution. The pristine and reduced samples were investigated using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and H_2-Temperature Programmed Reduction (TPR) to verify exsolution behavior. The perovskite oxides were used as fuel-electrodes in solid oxide cells. Cell test was conducted using Electrochemical Impedance Spectroscopy (EIS) and Linear sweep voltammetry (LSV).
Results and discussion. As the size of the exsolved nanoparticles increased, their shape changed from spherical to polymorphic (Fig. 1). Despite optimizing the reduction conditions and oxide composition, controlling the shape of exsolved nanoparticles in the porous electrodes remains challenging due to nonuniform growth resulting from the oxide powders with different sizes and surface orientations/terminations. To overcome this limitation, electrochemical reduction was used to maximize the growth of exsolved particles in the oxide electrode. As a result, the shape of the nanoparticles grown to over 50 nm changed from spherical to polymorphic. The exsolution electrode with shape-controlled unit cells exhibited high power/current density in both fuel cell and electrolysis applications. These results not only maximize the growth of exsolved nanoparticles but also provide a strategy for controlling the shape of exsolution electrodes.

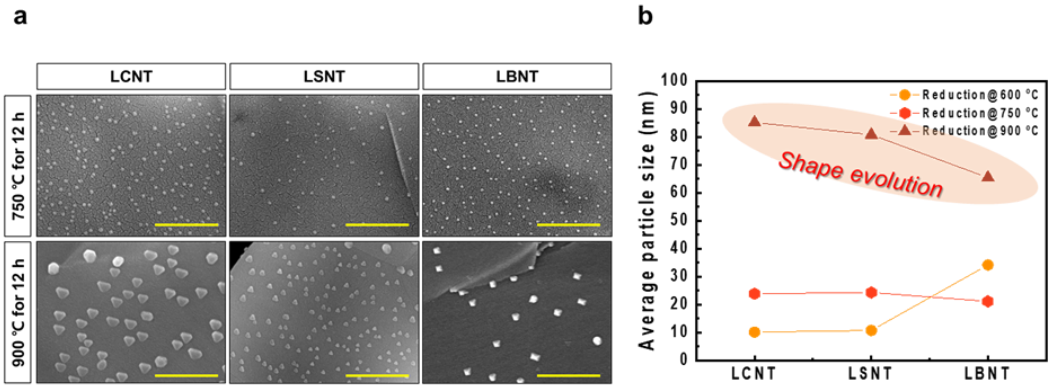

Fig. 1. Shape evolution of exsolved particles on reduced LMNTs. (a) SEM images of the reduced LCNT, LSNT, and LBNT at 750, 900 °C, respectively. (b) Average particle size of LCNT, LSNT, LBNT after reduction at 600, 750, 900 °C, respectively.

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Fabrication of Ultrathin PdAgPt Nanosheets by Controlling Composition for Enhanced Ethanol Oxidation Reaction

Jieun Yu, Jaehoon Jung*, Jongwook Hong*

Department of Chemistry, University of Ulsan, Ulsan, 44610, Korea
*jwhong@ulsan.ac.kr
*jjung2015@ulsan.ac.kr

Keywords: two-dimensional, ethanol oxidation, trimetallic, dendritic, electrocatalysis

Introduction.

Fuel cell systems such as DEFC are in the spotlight as promising future energy sources. Currently, Pt catalysts are mainly used in fuel cells. This is because Pt is heat resistant and does not corrode well. However, Pt is expensive. Pt also has poor stability due to adsorption with surface toxic substances. Therefore, various efforts are being attempted to improve these problems and develop nanoparticles with improved catalytic activity. Alloying metals and controlling morphology are promising ways to synthesize nanoparticles that have improved electrocatalytic activity and stability. However, it has not been reported much because it is difficult to synthesize structured multimetallic nanoparticles. Herein, we synthesized trimetallic 2D nanosheets alloying Pd and Ag on Pt by adjusting amount of surfactant and reductant. The particles we synthesized have an ultrathin 2D sheet structure. 2D sheets are efficient to use as catalysts because they have a structure with a maximized surface area. In addition, the synthesized nanosheets have a dendritic edge and are rich in undercoordinated atoms. The changed intrinsic activity of the undercoordinated atoms at the edge can adjust the degree of interaction with the reactants to improve EOR activity. Moreover, the nanosheets can be expected to have an ensemble effect due to the interaction through alloys of three types of metals. Since silver has an oxophilic property, it is helpful in generating surface OH_{ads} that prevent the generation of surface poisoning intermediates such as CO. We also synthesized nanoparticles with different compositions of metal to study the electrocatalytic activity of nanoparticles according to morphology and compositions. Through this, it was found that nanoparticles with a composition of $Pd_1Ag_1Pt_1$ have the most appropriate degree of adsorption with the reactant and have the highest activity in EOR.

Experimental/methodology.

To synthesize PdAgPt nanosheets, Pd, Pt, and Ag precursors were mixed with reductant and surfactant. The reaction solution was kept for 2 hours. The color of the solution containing nanosheets changed to black. By centrifugation 3 times, Nanosheets can be obtained. PdAgPt nanosheets with different compositions can be synthesized by controlling the volume of the metal precursors.

Results and discussion.

We synthesized trimetallic 2D nanosheets composed of Pd, Ag, and Pt. $Pd_1Ag_1Pt_1$ NSs with an ultrathin 2D structure were synthesized by adjusting the concentration of reductant and surfactant. X-ray diffraction (XRD) patterns and X-ray photoelectron spectroscopy (XPS) demonstrated that the synthesized nanosheets have an fcc crystal structure and a modified electron structure. We tested their electrocatalytic activity toward ethanol oxidation reaction, $Pd_1Ag_1Pt_1$ NSs showed the highest mass activity (10.442 mA mg^{-1}) and specific activity (27.4 mA cm^{-2}), compared to NSs with different compositions and commercial Pt/C catalysts, which attributed to their high surface area, many undercoordinated atoms, and optimized electronic structures. In the stability test, $Pd_1Ag_1Pt_1$NSs showed excellent properties due to the anti-toxicity, which corresponds to CO stripping test results.

In-situ Investigation of the MOF-Derived Catalyst Formation Mechanism

H. Haspel[1,2], T.G. Pocsai[3], D. Sebők[3], I. Szenti[1], D.G. Dobó[4], Á. Kukovecz[3], Z. Kónya[2,3*]

[1]*ELKH-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Szeged, Hungary*
[2]*Centre of Excellence for Interdisciplinary Research, University of Szeged, Szeged, Hungary*
[3]*Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary*
[4]*Institute of Pharmaceutical Technology and Regulatory Affairs, University of Szeged, Szeged, Hungary*
[*]*konya@chem.u-szeged.hu*

Keywords: coordination polymer, Metal-Organic Framework, MOF-derived catalyst, in-situ X-ray diffraction, X-ray microtomography

Introduction. Metal-organic frameworks (MOFs) gained significant attention as catalyst precursors, since presynthesized MOFs can be reduced, and transformed into supported metal nanoparticles at elevated temperature or in a reductive electrochemical environment [1]. One of the main benefits of the technique is the ability to form highly dispersed nanoarrays with well-defined active sites [2]. Furthermore, the high degree of dispersion is accompanied by high activities per metal atom in the resulting catalysts, even at high total metal content. It has previously been demonstrated that MOF-mediated synthesis (MOFMS) can also be realized through electro-decomposition, where the decomposition of a silver coordination polymer resulted in a highly active CO_2-to-CO electrocatalyst. However, despite of the thorough structural characterization of the resulting catalyst, the mechanism of formation remained unknown [3].

Experimental/methodology. Here, the same Ag coordination polymer (Ag-CP) was grown directly onto the carbon microporous layer of a carbon cloth gas diffusion layer by a sequential layer-by-layer (LBL) method via the spontaneous reaction of Ag^+ and an organic linker, 2,5-pyridinedicarboxylic acid. The Ag-CPs with different loadings were then decomposed into well-defined carbon-supported Ag structures at high temperatures in inert, reductive and oxidative atmospheres. The formation mechanism of the metal nanostructures was followed by in-situ X-ray diffraction (XRD), thermal methods (TGA, DSC), electron microscopy (SEM, TEM) and X-ray micro-computed tomography (µCT).

Results and discussion. Our current work focuses on the thermal decomposition of Ag-CP, where TGA showed two distinct weight loss regimes at around 290 and 550 °C under nitrogen. The former corresponded with the disappearence of Ag-CP reflections along with the emergence Ag reflections in the high-temperature in-situ XRD patterns (Fig. 1a). The morphology of the formed silver-based catalysts strongly depended on the number of deposition steps (Fig. 1b.), but the impact of several further parameters on the structure, morphology and elemental composition were also investigated. We hope that the detailed mechanism of MOF-derived catalyst formation will further advance a field of catalysis.

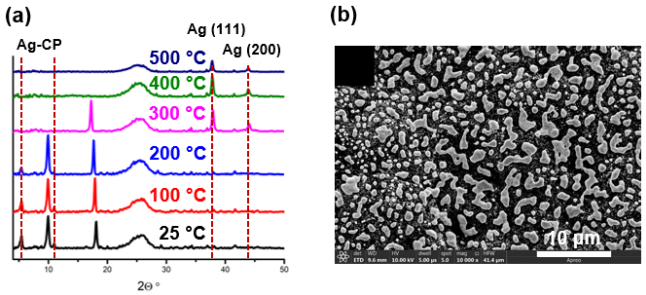

Fig. 1. *In-situ XRD patterns recorded during the transformation of carbon-supported Ag-CP into Ag/C at the indicated temperatures (a), and Ag/C from the decomposition of 7 layers of Ag-CP at 500 °C under N_2 (b).*

Acknowledgments
H.H. acknowledges the financial support of the János Bolyai Research Grant of the Hungarian Academy of Sciences (BO/682/22/7) and the New National Excellence Program of the Ministry for Culture and Innovation from NKFI Fund (ÚNKP-22-5-SZTE-574).

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Continuous high-throughput synthesis of Pt and Pt – Ni particles as fuel cell electrocatalysts using a Confined Impinging-Jet MicroReactor

Tanja Modl[1], Nicholas Lynn[1], Sabine Schmitz-Stöwe[1], Thomas Schwarz[1], Klaus Stöwe[1]

[1]*Chemnitz University of Technology, 09111 Chemnitz, Germany*
[*]*tanja.modl@chemie.tu-chemnitz.de*

Keywords: micromixer synthesis, MicroJet Reactor (MJR), Confined Impinging-Jet Microreactor (CIJMR), continuous-flow synthesis, precious metal nanoparticles, platinum nanoparticles, platinum nickel nanoparticles, core/shell nanoparticles, fuel cell catalysts

Introduction. In this contribution we report on an actual development in the field of fabrication and new application of micro-structured devices in chemistry enabling (multiphase) mixing, reactions and heat transfer which are not possible with standard devices. In the field of material syntheses micro-structured devices allow a strict control over process parameters offering the possibility to design materials with tunable properties such as particle size distribution, shape, composition and surface properties which contribute remarkably to the performance of catalytic materials [1].

Experimental/methodology. We implemented a new design of a CIJMR in the form of a cross mixing device analogous to the Synthesechemie (Dr. Penth) or Ehrfeld MicroJet Mixer (MJM) described by Dittert *et al*. [2]. The newly constructed MJR is completely dead volume free and allows the continuous preparation of nano-scale metal and metal chalcogenide particles by precipitation reactions from appropriate precursor solutions. Due to the short mixing times in the µs to ms range, crystallite nucleation and crystal growth are well separated from another and enable concentration limited particle growth and thus nanoparticle (NP) syntheses. To generate a deeper understanding of the processes within the MJR, modelling was performed by the CFD program ANSYS Fluent including chemical reactions (see Abstract K.Stöwe). Due to the flexibility of the concept the experimental setup can produce core-shell particles and other more complicated morphologies. It can also be broadened to syntheses in supercritical media as well as high-throughput approaches generating gradient libraries for high-throughput parameter screening.

Results and discussion. We started our research on the MJM with the syntheses of alternative support materials for fuel cell application to replace the standard carbon instable at typical operating conditions of PEMFC. Additionally, we applied this reactor concept by preparation of nano-scale sulfides, selenides and tellurides. We widened our expertise on precious metal NP in form of single element, mixed metal (alloys/intermetallic phases) or core-shell NP by investigating the system Pt – Ni. The stabilization of these particles was mostly achieved by chemical agents utilizing alkali metal hydroxides (Co4Cat process) [3]. As intended, the particle syntheses in the size range of 5 - 10 nm was successful while the stability of these particles was verified to be at least 10 weeks. Additionally, we also extended the reactor system and currently use a second MJR in series of the first reactor for the syntheses of either Ni@Pt or PtNi@Pt - NP. These particles are in the focus for applications as fuel cell electrocatalysts in the BMWK-funded project "ISyKat".

All in all, we will present a significant contribution for the development of new approaches for a more effective synthesis and screening of new functional materials for industrially relevant applications.

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Fabrication and charcteristics of MXene for the secondary battery

K. M. ROH[1*], S. K. Kim[1], T. J. Park[1], H. J. Kwon[2,] J. J. You[3]

[1]*Korea Institute of Geoscience and Mineral Resources, Daejeon, Republic of Korea*
[2]*Jeonbuk National University, JeonJu, Republic of Korea*
[3]*Korea Institute of Energy research, Daejeon, Republic of Korea*
[*] *kmroh@kigam.re.kr*

Keywords: MXene, MAX, Secondary battery

Introduction. Recently, Mxene, a two-dimensional transition metal compound, has been emerging as a new material in the field of in electrocatalysts, optical sensors, electronics, biomedical, electromagnetic, and energy storage devices because of metal-like electrical conductivity, ion adsorption and high chemical stability.[1-3] Based on these advantages, MXenes are used and tested for various applications, particularly in developing secondary battery techniques for advanced smart systems, electric cars and energy stroage sytmes.[4-9] There have been remarkable research achievements in the synthesis and application of MXene-based materials with new synthesis routes and novel structures. Herein, we demonstrate a fabication process of vandium MXene and its electircal charcteristics for the secondary battery.

Experimental/methodology. The basic mixing conditions were set to 2:1.2:0.8 in the molar ratio of V, Al, and C for the formulation of Max with vanadium metal as a raw material. For uniform mixing and MAX synthesis experiments, a ball mill mixing for 24 hours was conducted. To increase the reactivity between V, Al, and C during the heat treatment process, uniformly mixed raw materials are made into 50mm circular pellets through uniaxial compression and heat treatment is performed. For the etching chemical reaction of MAX, 10 g of MAX V_2AlC was added to HF (100 ml) and reacted at 45 ℃ for 72 hours. Through an etching chemical reaction, the Maxine layer of the two-dimensional shape is peeled off, and the vanadium-based Maxine V_2CT_x is recovered as an intermediate material.

Results and discussion. As a result of XRD analysis of the finally manufactured V_2CT_x, it was confirmed that a clear 2D peak appeared at about 7 degrees, verifying that V_2AlC MAX was successfully exfoliated into V_2CT_x MXene. From the AFM analysis results, it was confirmed that the MXene sheet had a thickness of about 2 nm or less. Constant current charge/discharge electrochemical experiments were performed on the coin cells manufactured using MXene in an aqueous electrolyte of 3 M $ZnSO_4$. The synthesized vanadium MXene-based anode showed an initial discharge capacity of 126 mAh/g at a current density of 0.1 A/g, and a maximum capacity of 145 mAh/g was achieved in the initial 5 cycles. As the cycle progresses, the capacity decreases to 130 mAh/g, 89% life stability and >99% coulombic efficiency was shown up to 100 cycles.

Acknowledgments
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Environmental photocatalysis

Cross-dimensional activation of 2D cobalt hydroxide with 0D cobalt oxides for photocatalytic microplastic degradation

R. Greco[1*], F. Temerov[1], W. Cao[1]

[1] *Nano and Molecular Systems Research Unit, University of Oulu, FIN-90570, Finland.*
[*] *Rossella.Greco@oulu.fi*

Introduction. The degradation of water pollutants by heterostructured photocatalysts has seen a great development during the last decades [1]. Indeed, the synthesis of composite photocatalysts solves two of the most highlighted drawbacks of photocatalysts, i.e., electron-hole recombination and visible light inactivity [2]. In addition, the use of photocatalysts enhances the formation of $OH^{\bullet}$ or $O_2^{\bullet-}$, fundamental for the advanced oxidation processes (AOPs) at the basis of the breakdown of covalent bonds in the organic molecules forming the pollutants [3]. Nowadays, microplastics (MPs), defined as plastic particles with a size lower than 5 mm [4], are some of the most worrying water contaminants [5]. One of the possible approaches for decreasing these entities in natural environment is the photodegradation. In this case, the polymer is converted to smaller molecules, which might be useful for subsequent reactions [6]. Up to now, few studies have been carried out on photodegradation of MPs and mainly by using TiO_2 [7], which is known to be unactive in visible light. Consequently, there is a need of new materials applied in this field and composites possess high applicability in the MPs degradation [6b, 8] due to the possibility of overcoming the most common disadvantages of photocalysts.

Experimental/methodology. For the synthesis of the composite Co_3O_4@$Co(OH)_2$, an hydrothermal one-pot method was used and, by changing the pH or the temperature, the isolated components (Co_3O_4 and $Co(OH)_2$) could be obtained. Finally, the obtained solids were characterized by using different techniques, i.e., XRD, XPS, SEM, TEM, among others. Then, the catalyst was added to an aqueous suspension of polystyrene MPs at a concentration of $2.5 \cdot 10^{-3}$ w/v %. After irradiation with a white light LED, the microplastics photodegradation was evaluated by SEM and weight loss and the formation of products by LC-MS.

Results and discussion. In this work, we could perform the one-pot synthesis of 0D/2D composite Co_3O_4@$Co(OH)_2$ and the two isolated components of the composite could be obtained by modulating the synthetic conditions. The composite showed activity in the photodegradation of MPs in water, meanwhile the hydroxide and the oxide had no activity in the above-mentioned reaction, demonstrating the relevance of the use of the composite. Indeed, compared to the original components, the hybrid material has different electronic structure, which makes the material more suitable for the photodegradation due to a better separation of the charge carriers, as demonstrated by photocurrent measurements, and allowing the formation of the radicals involved in the degradation as demonstrated by EPR.

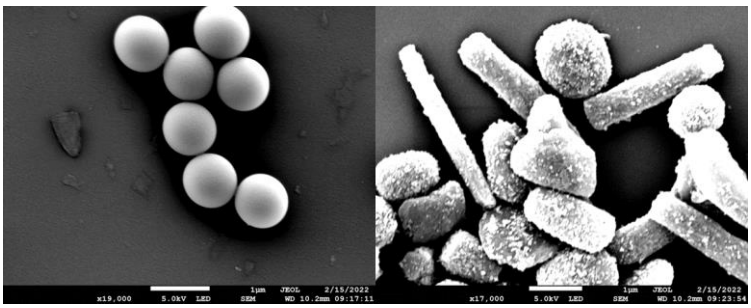

Figure 1. Polystyrene MPs before (right) and after (left) the photodegradation process with Co_3O_4@$Co(OH)_2$

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Continuous in situ measurement of photocatalytic efficiency of powder materials in liquid dispersions by optical absorption method

R. Dvorsky[1,2,3*], L. Svoboda[1], J. Bednář[1], Z. Vilamová[1,3], Z. Šimonová[1,4,5]

[1]*Nanotechnology Centre - CEET, VSB – Technical University of Ostrava, Ostrava, Czech Republic*
[2]*Centre for Advanced Innovation Technologies, VSB – Technical University of Ostrava, Ostrava, Czech Republic*
[3]*Faculty of Materials Science and Technology, VSB – Technical University of Ostrava, Czech Republic*
[4]*IT4Innovations, VSB – Technical University of Ostrava, Ostrava, Czech Republic*
[5]*Department of Machining, Assembly and Engineering Metrology, Faculty of Mechanical Engineering, VSB-Technical University of Ostrava, Ostrava, Czech Republic*
[*]*richard.dvorsky@vsb.cz*

Keywords: photocatalysis; in situ measurements; reactor design, optical absorption; TiO_2

Introduction. The photocatalytic activity of materials still cannot be determined by molecular simulations. Therefore, all photocatalytic activity of the materials is determined experimentally in laboratories. However, existing standard measurements are not free from disadvantages and the whole measurement is time-consuming [1–3]. The aim of this work was to design a new method for in situ measurements and to construct a new photocatalytic reactor, thus eliminating expensive laboratory equipment for testing photocatalytic activity, as well as several disadvantages, including the time-consuming process of testing photocatalytic activity.

Experimental/methodology. The in situ measurement method is based on a newly derived modification of the absorption Lambert-Beer law, which takes into account not only absorption but also light scattering on dispersed nano/microparticles and a new design of the photocatalytic reactor. For all experiments, the concentrations were set as TiO_2 P25 (c = 1 g.L^{-1}), methylene blue (MB) (C_o = 0.001 g.L^{-1} , V = 150 ml), source of radiation was 10 W high-power 365 nm LED chip. Experimental conditions were set in such way to avoid the photosensitization phenomenon.

Results and discussion. The functionality of the new method was demonstrated on the decomposition of methylene blue using TiO_2 P25 powder and 365 nm wavelength radiation according to ISO 10678 [3]. Comparison of two independent experimental measurements with each other and with a subsequent comparison using a standard method for the evaluation of photocatalytic activity confirmed the accuracy and good repeatability of the new in situ measurement method, without distortion of the observed kinetics data due to the presence of the photocatalyst, see Figure 1.

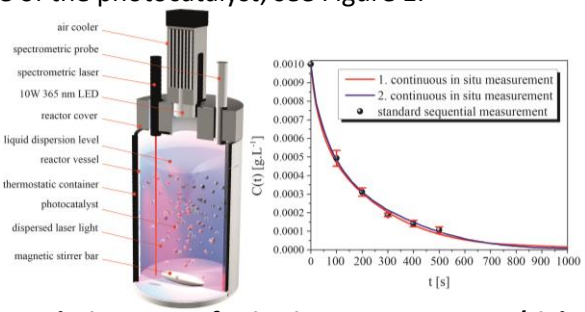

Figure 1 (left) Novel photocatalytic reactor for in situ measurement. (right) Comparison of two independently measured simulant concentration versus time dependencies (— 1. measurement and — 2. measurement) with six points obtained by standard photocatalytic measurement method.

Acknowledgments
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Layer-by-layer self-assembled TiO_2 and plasmonic Ag@TiO_2 hybrid nanoscale transparent thin films for gas phase photocatalysis

M. Motay,[1,2] L. Ploux,[3] L. Balan,[4] C. Colbeau-Justin,[5] G. Decher,[2] N. Keller[1*]

[1] *ICPEES, UMR 7515 CNRS/Strasbourg University, Strasbourg, France*
[2] *Institut Charles Sadron, CNRS/University of Strasbourg, Strasbourg, France*
[3] *BIOMAT (U1121 INSERM/Université de Strasbourg), Strasbourg, France*
[4] *CEMHTI-CNRS UPR3079, Orléans, France*
[5] *Institut de Chimie Physique, CNRS UMR 8000, Université Paris-Saclay, France*
[*] *nkeller@unistra.fr*

Keywords: Layer-by-layer (LbL), plasmonic photocatalytic films, photoinduced synthesis, air treatment

Introduction. The LbL assembly method has received a growing interest in the last decades to design function-specific multilayer assemblies like catalytic thin films. It easily builds versatile multi-material films with tunable properties at nanoscale precision. The films are built via electrostatic interactions, by alternate deposition of oppositely charged species on a substrate, previously negatively or positively charged [1].

Here we show the promise of the LbL self-assembly for building porous, stable TiO_2 and plasmonic Ag@TiO_2 hybrid nanoscale films with a very good growth monitoring (thickness, homogeneity, catalyst content). We demonstrate that a catalyst-saving film with a single nm-size hybrid layer of TiO_2 and Ag nanoparticles at ultra-low TiO_2 content is highly promising for gas phase photocatalysis aiming at air depollution.

Experimental. For building multilayer PEI/(PSS/TiO_2)$_n$ films on model surfaces (quartz slide or Si wafer), positively-charged poly(ethyleneimine) (PEI) is used as an anchor polyelectrolyte to promote the film adhesion. Negatively-charged poly(sodium 4-stryresulfonate) (PSS) is deposited on the PEI layer and acts as a glue between consecutively deposited TiO_2 layers. In order to preserve the TiO_2 positive surface charges, PSS is dissolved in acidic milli-Q water. The LbL-assembled films are built by dipping successively the substrate in the polyelectrolyte solution or in the TiO_2 suspension, with intermediate rinsing with water.

Results and discussion. The LbL film growth is monitored on model surfaces by ellipsometry, in-situ quartz crystal microbalance, UV-Vis spectroscopy, AFM/SEM. It shows regular film growth with average thickness increase of 40 nm and TiO_2 density of 6 ± 1 µg/cm² per layer pair. The PEI/(PSS/TiO_2)$_n$ films show very good homogeneity, even for a single layer pair, *ie.* PEI/(PSS/TiO_2), and good porosity, allowing the TiO_2 crystallites to be available for the gaseous pollutant. They remain transparent, at least till n=10 layer pairs [2].

Ag@TiO_2 catalyst films were built on model surfaces by a new integrated *one-pot* approach combining a photoinduced radicalar synthesis of calibrated Ag nanoparticles (AgNP) and the LbL assembly of TiO_2 thin films. The AgNP photoinduced synthesis lies in the irradiation of a photosensitive formulation, where a chromophore acts as free radical generator upon UV-A light (365 nm). One free radical allows the reduction of Ag^+ to Ag^0 which associates further into clusters and forms AgNP, while a second radical controls size and shape. The key-point here is the use of the photosensitive formulation as LbL solvent for depositing the TiO_2 layer. It allows building single layer pair Ag@TiO_2 films with well-calibrated (2 nm) small size AgNP with narrow distribution, in intimate contact with the TiO_2 crystallites. The Ag/TiO_2 ratio can be tuned on-demand and the AgNP are located at the PSS/TiO_2 interface while the films remain transparent.

Optimized PEI/(PSS/Ag@TiO_2) thin films with Ag/TiO_2 ratio of 0.25 wt.% led to a drastic increase in TONs (16 fold) compared to the Ag-free reference film, with a quantum (photonic) yield increase of one order of magnitude. The catalytic film obtained by the one-pot photoinduced approach outperformed strongly PEI/(PSS/Ag@TiO_2) films obtained via other methods. Thanks to Time Resolved Microwave Conductivity, Electron Paramagnetic Resonance and UV-vis spectroscopy, the generation of a higher number of charge carriers was evidenced, what supported the hypothesis of a plasmonic near-field enhancement, thanks to the overlap of the AgNP plasmonic band and the catalyst absorption.

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Effect of tunable shell thickness on the plasmon-enhanced photocatalytic activity of Au@TiO_2 core-shell nanoparticles

R.Ninakanti[1,2*], R. Borah[1], S. Bals[2], S.W. Verbruggen[1]

[1]*(DuEL), University of Antwerp, Antwerp, Belgium*
[2]*(EMAT) University of Antwerp, Antwerp, Belgium*
[*]*Rajeshreddy.ninakanti@uantwerpen.be*

Keywords: core shell nanoparticles, plasmonic photocatalysis, electromagnetic near-field enhancement

Introduction.

The use of gold and silver nanoparticles to boost the activity of TiO_2 based photocatalysts by exploiting their plasmonic effect, has become a widely applied strategy to improve various solar light driven applications, such as photocatalytic air purification, self-cleaning surfaces, etc [1,2]. However, plasmonic metal nanoparticles like Au sinter together when treated at elevated temperatures, which is often required to calcine TiO_2 into the appropriate anatase phase. Here, these limitations are overcome by stabilizing plasmonic Au nanoparticles through the formation of a thin and uniform TiO_2 shell, that also directly acts as the semiconducting photocatalyst. The dependence of the plasmonic near-field enhancement on the TiO_2 shell thickness surrounding the Au core is further substantiated by means of surface enhanced Raman spectroscopy (SERS) using a probe of R6G molecules on Au@TiO_2 thin films.

Experimental/methodology.

The synthesis of gold nanoparticles (~55 nm) is a process based on the protocol in [3]. Encapsulation of Au nanoparticles with TiO_2 was performed with slight modifications based on procedure described in [4]. The material was characterized using HAADF-STEM, UV-Vis spectroscopy, SERS, XRD and theoretical electromagnetic simulations. Stearic acid degradation was performed to check photocatalytic activity using simulated light

Results and discussion.

In this work, Au@TiO2 core-shell nanoparticles have been studied by carefully varying the shell thickness at the nanometer scale. Slow hydrolysis of the titanium triethanolaminato isopropoxide precursor proved to be the key to accurately control the thickness of this TiO2 shell. Photocatalytic stearic acid degradation tests revealed that the photocatalytic activity decreases by a factor of 2 when increasing the shell thickness from 2 nm to 15 nm. This agrees with Finite Element Method numerical simulations that demonstrate that near-field enhancement, one of the main driving plasmonic effects, rapidly decays over just a few nanometers from the surface of a metal nanoparticle [5]. A significant reduction in enhancement factor of SERS for a thicker TiO2 shells does invariably prove plasmonic nanoparticles with thinner shell thickness benefit from a stronger contribution from near-field enhancement for photocatalysis. At the same time, a minimal shell thickness is required to ensure sufficient stabilization of the metal cores upon thermal annealing, as is studied by high resolution transmission electron microscopy. Results of photocatalytic activity in combination with SERS experiments and numerical simulations, prove that nanometer control over the shell thickness can lead to the most efficient use of the near-field enhancement effect of plasmonic nanoparticles in photocatalytic applications.

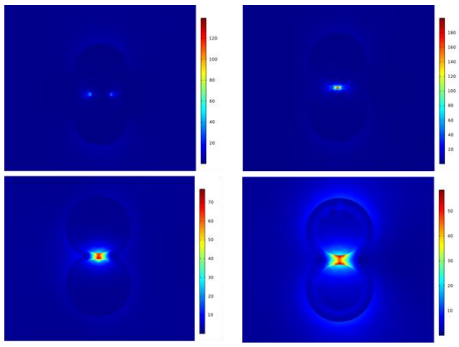

Figure 1 Near field enhancement maps of a. Au2, b. Au5, c. Au8 and d. Au12 at the wavelength of LSPR.

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Photocatalytic efficiency of VOC removal on TiO_2 nanotubes: Effect of layer thickness

J. Rusek, M. Baudys, M. Lhotka, J. Krýsa

Department of Inorganic Technology, University of Chemistry and Technology Prague, Czech Republic

Keywords: TiO_2, nanotubes, photocatalysis, volatile organic pollutants, hexane

Introduction:

TiO_2 nanotubes (TNT) seem to be an interesting photocatalytic material due to the high surface area and geometry enabling better separation of photogenerated charges [1]. This contribution deals with the preparation and characterization (morphology, texture properties) of TNT layers of different thickness. The objective was to find the relation between morphology, surface area and photocatalytic activity which was determined using hexane and acetaldehyde as model gaseous pollutants in a flow-through photoreactor.

Experimental/methodology:

TNT layers were prepared by anodic oxidation of Ti foil using a previously optimized procedure based on the work [2]. Prepared samples were characterized using SEM and also using Kr adsorption isotherm (expressed as adsorbed amount related to the geometric area). The photocatalytic activity was expressed as a conversion of hexane (acetaldehyde) using conditions according to the ISO 22197-2 standard method.

Results and discussion:

The thickness and photocatalytic properties of TNT layers, varying in anodization time, are summarized in Table 1. As expected, the nanotube thickness increased with increasing anodization time from approximately 2 to 13 µm. Typical morphology of the TNT layer is shown in Fig. 1, with a tube diameter ~100 nm and wall thickness 6-8 nm.

Table 1: Thickness and photocatalytic properties of the TNT layers depending on anodization time.

anodization time (min)	TNT thickness (µm)	hexane conversion (%)
15	2.3 ± 0.1	18
45	4.3 ± 0.2	25
90	10.3 ± 0.8	27
120	13.2 ± 0.5	29

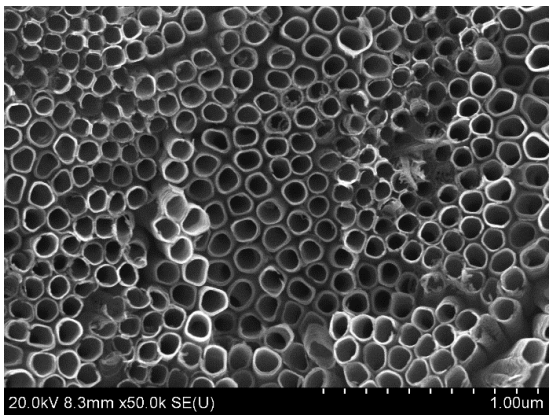

Fig 1: SEM micrograph of the top morphology of the TNT layer prepared by anodization for 45 min.

From TNT diameter and wall thickness, the geometrical area and the mass of TiO_2 for various TNT layers were calculated. Using Krypton adsorption isotherm (related to the geometric area), it was found that adsorbed amount increased with increasing TNT thickness. BET surface area, calculated from Kr adsorption, was for TNT layers of all thicknesses approximately 30 $m^2\ g^{-1}$. An increase of hexane conversion with TNT thickness from 18 to 29 % was discussed in view of increased surface area (either from TNT geometry or Kr adsorption measurement).

Acknowledgments

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Role of metal nanoparticles in non-oxidative methane coupling to ethane using a novel gas flow-through photocatalytic reactor

V. Longo[1*], L. De Pasquale[1], F. Tavella[1], S. Perathoner[1], G. Centi[1], C. Ampelli[1], C. Genovese[1*]

[1]*University of Messina (Dept. ChiBioFarAm), ERIC aisbl and CASPE/INSTM, V.le F. Stagno d'Alcontres, 31, 98166 Messina, Italy*

**victor.longo@studenti.unime.it; chiara.genovese@unime.it*

Keywords: methane photo-coupling, gold, titania**,** flow reactor

Introduction. The Development of technologies for methane valorisation to more useful carbon products is highly desirable but conventional thermocatalytic routes require a high temperature to break the strong C–H bond [1]. In this perspective, the direct photocatalytic non-oxidative coupling of methane (NOCM) has attracted research as it is possible to convert solar energy in chemicals in mild conditions avoiding the competitive and thermodynamically more favourable formation of coke. Currently, the majorities of photocatalytic methane coupling reactions are carried out in batch reactors but generally the performances are very low**.** In this work we have reported a continuous photocatalytic NOCM process using a new concept of flow reactor, with metal-decorated TiO_2 nanomembranes as photocatalysts [2]. The presence of a cocatalyst is crucial for promoting the activity of the semiconductor increasing the performances of photocatalytic CH_4 conversion [3].

Experimental. The metal nanoparticles (NPs) decorated TiO_2 (Au, Ag, Pd,) photocatalysts were prepared through photo deposition method irradiating standard TiO_2 P25 under UV light for 30 min. The amount of all metals was in 1% w/w. The as prepared samples were characterized by SEM. XRD and UV-vis analysis, were then deposited in a porous membrane and tested in the NOCM in a home-made cross-flow reactor equipped with a quartz window to allow the illumination (300W Xe lamp). The gaseous methane passes through the photoactive nanomembrane. Only one side is illuminated. The products were analysed by GC equipped with FID and TCD detector.

Results and discussion. In the present work different metals were examined for NOCM at ambient conditions (room temperature and atmospheric pressure), using a concept of reactor (working under a gas cross-flow) quite different from a conventional photocatalytic approach. The synergistic effect of combining this new flow reactor with a suitable cocatalysts was investigated. Results show that, among all metal NPs examined, Au is the most efficient in ethane production. Localized Surface Plasmon Resonance (LSPR) of Au NPs simultaneously accelerate the charge separation improving the light absorption in TiO_2 semiconductor, pushing the methane photo conversion and suppressing the overoxidation of CH_4 due to lattice oxygen of the support. The ethane production rate reached 95.3 micromol $g^{-1}h^{-1}$ in 5 hours of reaction with 50% of methane and a high selectivity to C_2 products was observed (>95%). The photocatalytic activity of Au/TiO_2 is two orders of magnitude higher than that of pure porous TiO_2. Blank tests were also performed, and no products have been detected when the reaction was carried out in inert gas or without light irradiation Due to the particular characteristics and conditions in the photoreactor, by combining it with the LSPR of Au nanoparticles, the efficiency in non-oxidative coupling of methane has been much improved.

Acknowledgments

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Photocatalytic cleavage of lignin C–C bonds

X. Wu,[1] S. Xie,[2] Y. Wang[2] and B. F. Sels[1]*

[1]*Center for Sustainable Catalysis and Engineering, Faculty of Bioscience Engineering, KU Leuven, Heverlee 3001, Belgium.*
[2]*State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.*
**bert.sels@kuleuven.be*

Keywords: Photocatalysis; Lignin; C–C bond cleavage; radical intermediates

Introduction. Lignin is a major component of lignocellulosic biomass and a natural aromatic biopolymer, and thus, it is the most abundant source of renewable aromatics.[1] Through selective breakage of lignin C−O, C−C bonds, added-value aromatic compounds can be obtained.[1] Great efforts have been devoted to the study of lignin C−O bond cleavage in past decades and considerable success has been achieved.[1,2] In contrast, only a few research progress has been made in the selective cleavage of lignin C−C bonds. The cleavage of recalcitrant C−C bonds remains one of the key challenges for the valorization of lignin. Current studies on lignin C−C bond cleavage are mainly focused on thermocatalysis under relatively severe reaction conditions.[3] The conventional methods not only limit the activity but also lead to low product selectivity. Moreover, additional additives such as expensive oxidants or bases are needed in most cases.[3] Photocatalysis, which utilizes solar energy to drive chemical reactions as nature does for photosynthesis, is a promising method to challenge highly difficult reactions by conventional thermocatalytic approaches.[4] However, as a newly emerging and challenging topic, only a few reports have succeeded in breaking lignin C−C bonds by photocatalysis. Moreover, the current understanding of the reaction mechanisms and the knowledge about the photocatalyst structure-performance relation are very limited.

Results and discussion. We examined photocatalytic performances of some typical semiconductors including $BiVO_4$, Cu_2O, CeO_2, BiOCl, BiOI, CdS, and PCN for the conversion of 1,2-diphenylethanol (DPol), a lignin β-1 model compound, at room temperature. Limited activities with conversion lower than 5% were observed for most catalysts. Interingtly, PCN is very unique in catalyzing the cleavage of the C_α−C_β bond in DPol, benzaldehyde is the major product with a high selectivity of 68% and yield of 15% after 6 hours under simulated solar light irradiation. To increase the photocatalytic performance of PCN, we have synthesized a series of Ag_3PO_4−PCN heterojunction nanocomposites. Among these nanocomposites, 40Ag_3PO_4−60PCN (40wt% Ag_3PO_4−60wt% PCN) showed the highest benzaldehyde yield, reaching 86%, which was about 5.7 times higher than that of PCN. 40Ag_3PO_4−60PCN nanocomposites were powerful catalysts for photocatalytic cleavage of lignin C_α−C_β bonds. Aromatic aldehydes with high yields of 66%-95% were obtained from the conversion of various β-1 lignin model compounds.

Characterizations of the catalysts led to structural details of the Z-scheme within Ag_3PO_4−PCN composites. Control experiments with different atmospheres, *i.e.*, O_2 and N_2, and additives, *i.e.*, $Na_2C_2O_4$ as a hole scavenger, $NaIO_3$ as an electron scavenger, *i*-PrOH as a hydroxyl radical scavenger, and BQ (p-benzoquinone) as a superoxide radical scavenger, were performed. These control experiments have revealed three reaction pathways for the conversion of DPol. The primary pathway involves an electron-hole coupled photoredox process, which requires both holes and electrons with strong oxidation and reduction ability, respectively. The Z-scheme structure allows the Ag_3PO_4−PCN catalyst to have strong redox capacity and this is essential to the electron-hole coupled C−C bond cleavage.

Acknowledgments
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TiO_2 and CeO_2 systems modified with photo-reduced graphene oxide for photocatalytic applications

S. A. Balsamo[1*], R. Fiorenza[1], S. Scirè[1]

[1]*Department of Chemical Sciences, University of Catania, Catania, Italy*
[*]*stefano.balsamo@phd.unict.it*

Keywords: Photocatalysis, water remediation, Hydrogen, Graphene oxide

Introduction. Water remediation and H_2 production are two of the most pressing topics in photocatalysis. The most common material in this field is the titanium dioxide (TiO_2, titania), but the performance under the solar light must be improved. Furthermore, after the addition of the titanium in the EU critical raw materials, it is necessary to find alternatives to the titania and, in this context, the excellent redox properties of the cerium dioxide (CeO_2) can be a good solution. However, despite the lower band gap respect to the TiO_2, the CeO_2 has a really high charge recombination rate, so a modification, in order to avoid this phenomenon, it is mandatory. Amongst the strategies to enhance the charge separation, the employing of carbonaceous materials as the graphene oxide can be a perfuming strategy thanks to its peculiar properties such as high conductivity and visible light absorption in its reduced form (reduced graphene oxide, rGO). Thus, to make it capable to extend the charge separation lifetime and to absorb the solar radiation [1]. Here we report a method for a one-pot solar photo-reduction of the GO by TiO_2 or CeO_2, obtaining versatile hybrid materials [2]. The synthetized samples were tested on water remediation degrading a pesticide (the 2,4 dichlorofenoxyacetic acid) and in the H_2 production through glycerol photoreforming.

Experimental/methodology. The samples were prepared irradiating a GO solution in presence of the main catalyst (TiO_2 or CeO_2) in anaerobic condition. In the case of the H_2 production, a gold precursor was added in order to exploit a metallic co-catalyst. The materials were investigated in terms of rGO content, reduction degree and irradiation time employed for the reductive treatments. To achieve this characterization, were used UV-DRS, FTIR, PL, XPS, SEM and TEM images and finally BET surface area.

Results and discussion. The TiO_2-rGO composites showed the best results in terms of activity in the 2,4-D degradation (97% of degradation in three hours vs the 48% of the bare TiO_2 or the 60% of the conventional thermal reduced TiO_2-rGO, Fig, 1a). For the hydrogen production (Fig. 1b) it was obtained an increment of about 8 times with the TiO_2-based samples and about 40 times with the CeO_2-based ones compared to the bare TiO_2 and CeO_2. In this context, the photocatalytic activity is strongly influenced by the reduction degree of the GO, that in the case of TiO_2-based samples was favored by the strong photocatalytic features of titania, whereas in the case of ceria-based samples was facilitated by the continuous irradiation time.

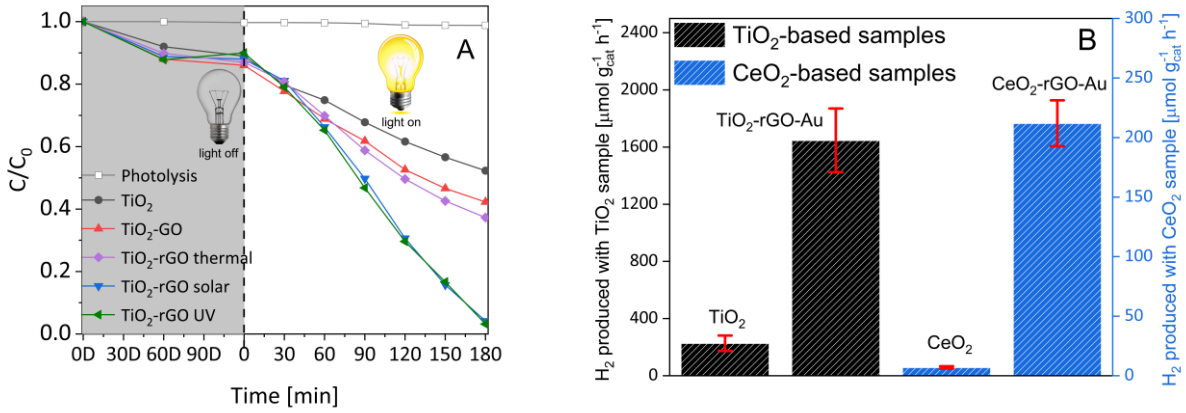

Figure 1 In the left panel the photodegradation results, while in the right one the H_2 evolution after 6h

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Carbon spheres modification and activation for CO_2 capture and utilization

E. Kusiak-Nejman[1], F. Latzke[1], K. Ćmielewska[1], A. Wanag[1], J. Kapica-Kozar[1], E. Ekiert[1], I. Pełech[1], A.W. Morawski[1], U. Narkiewicz[1]

[1]*West Pomeranian University of Technology in Szczecin, Faculty of Chemical Technology and Engineering, Department of Inorganic Chemical Technology and Environment Engineering, 70-322 Szczecin, Poland*
[*]*Corresponding Author's E-mail address: ekusiak@zut.edu.pl*

Keywords: carbon sprehes, metal oxides, aminosilanes, CCU, adsorption, CO_2 photoutilization

Introduction. Worldwide carbon dioxide emissions of 34.9 $GtCO_2$ in 2021 resulted in an increase of 4.8% over the year 2020, while the Global Carbon Project report put the increase in global emissions in 2022 at 36.6 $GtCO_2$ [1,2]. While promising, technologies such as carbon capture and storage (CCS) and carbon capture and utilization (CCU) require continuous development and increased operational coverage. CCU facilities capture almost 45 $MtCO_2$ per annum. However, despite such impressive achievements, Net Zero Emissions may not be reached at these technologies' current rate of advancement [3]. Carbon dioxide can be converted to valuable chemicals (like methanol, formic acid or methane) in several technological approaches, of which the most developed are: catalytic, photocatalytic, electrochemical, biological and mineralization [4].

Experimental/methodology. Sample preparation methods: carbon spheres formation according to modified Stöber method (from resorcin and formaldehyde) and heat treated at 700 °C, activation with various chemical agents (selected bases and salts), carbon spheres modification with metal oxides (mainly TiO_2) and/or aminosilanes (APTMS, APTES etc.). Sample characterization methods: SEM-EDX, TG/DTG, XRD, FTIR, low-temperature N_2 adsorption/desorption (BET specific surface area, pore volume), CO_2 adsorption/desorption (ultramicropore volume and distribution, adsorption capacity).

Results and discussion. The unmodified carbon spheres obtained as part of the ongoing studies were characterized by a high adsorption capacity towards CO_2 (due to the highly developed specific surface area and the predominance of ultramicropores in the structure of the carbon materials). However, their photocatalytic activity was negligible (the photolysis effect works only). Activation of unmodified carbon spheres with alkalis and salts resulted in a significant increase in specific surface area and the development of a porous structure in the micro- and ultramicroporous range, translating into increases in CO_2 adsorption capacity, while CO_2 photoreduction efficiency remained low. Solvothermal, microwave-assisted or thermal modification of carbon spheres with semiconductors or aminosilanes resulted in a reduction in specific surface area and pore volume (due to blocking of pores by nano-TiO_2 or aminosilane molecules), which slightly reduced the CO_2 adsorption capacity, but on the other hand, definitely increased the efficiency of the CO_2 photoreduction. Hydrogen, carbon monoxide, and methane were mainly formed photoreduction products. Under specific conditions, green ammonia formation was found.

Acknowledgements
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Selective and Efficient Photocatalytic Reduction of 3-Nitrophenol to 3-Aminophenol by Anatase and Rutile TiO_2 – What Stands Behind the Photoactivity?

Kasidid Yaemsunthorn,[1] Wiktoria Adamowicz,[1,2] Marcin Kobielusz,[1*] Wojciech Macyk[1*]

[1]*Faculty of Chemistry, Jagiellonian University, ul. Gronostajowa 2, 30-387 Kraków, Poland*
[2] *Doctoral School of Exact and Natural Sciences, Jagiellonian University, ul. Łojasiewicza 11, 30-348 Kraków, Poland*
[*]*kobielusz@chemia.uj.edu.pl, macyk@chemia.uj.edu.pl*

Keywords: Photocatalysis, 3-nitrophenol reduction, titanium dioxide

Introduction

The reduction of nitroaromatics is a common route to producing aminoaromatics. Amines, especially aniline derivatives are precursors of many valuable organic molecules with a wide range of applications. Nowadays, they are mainly obtained by hydrogenating the corresponding nitroaromatics. Nevertheless, the process can be demanding for functionalized nitro compounds containing unsaturated bonds. It has recently been shown that the photocatalytic reduction of nitroaromatic compounds to amines occurs with high selectivity even in the presence of various sensitive groups.[1] In such a reaction, TiO_2 is often considered as the photocatalyst. However, no studies so far explored what factors limit this process for TiO_2. We investigated the correlation between several intrinsic factors and the photocatalytic activity of various commercial anatase and rutile TiO_2 materials for the selective reduction of 3-nitrophenol.

Results and discussion

The (photo)electrochemical analysis revealed unequivocally the differences in interfacial electron transfer, charge recombination, reduction driving force, and methanol photooxidation efficiency for titania polymorphs. It appeared that all mentioned processes were phase-dependent and they contributed unequally to overall photocatalytic activity (Fig. 1.). In particular, methanol oxidation was the most efficient at the rutile phase, which overcame the critical limitation of the oxidation pathway and facilitated the reduction of 3-nitrophenol. On the other hand, the dark electron transfer efficiency was highest at the anatase phase, despite the lower driving force in this case. A thorough and systematic analysis of the discussed photocatalytic system (the photocatalyst and the reaction) will be presented.

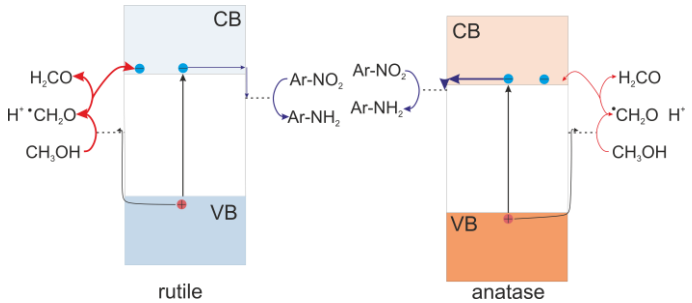

Fig. 1. Photocatalytic reduction of nitroaromatics with highlighted differences between rutile and anatase. The thickness of the arrows refers to the efficiency of the corresponding processes.

Acknowledgements

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The Design of New $SrTiO_3$-based Catalysts for Photocatalytic CO_2 Reduction Applications

B. Boga[1,2*], N.G. Moustakas[1], P. Naliwajko[1], A.B. Ngo[1], S. Ding[1], T. Peppel[1], N. Steinfeldt[1], V.M. Cristea[2], J. Strunk[1§]

[1]*Leibniz Institute for Catalysis, Rostock, Germany*
[2]*Babeș-Bolyai University, Cluj-Napoca, Romania*
**biborka.boga@catalysis.de, §jennifer.strunk@catalysis.de*

Keywords: photocatalytic CO_2 reduction, surface plasmonic effect, CO_2 adsorption, $SrTiO_3$-$SrCO_3$, NiO

Introduction. The world energy demand and the increasing atmospheric CO_2 concentration are current problems which require urgent actions [1]. Photocatalytic CO_2 reduction could be a promising solution for the aforementioned challenges, which is based on the design and application of highly efficient and selective photocatalyst materials. Beyond charge carrier generation and separation, CO_2 adsorption ability is also a decisive property towards efficient photocatalysts for CO_2 reduction [2], and it must be taken into account during catalyst design. In this work, the influence of Au photodeposition and NiO impregnation of $SrTiO_3$-$SrCO_3$ catalysts on their photocatalytic CO_2 reduction activity was studied.

Experimental/methodology. Herein four catalysts were prepared and assessed, namely hydrothermally synthesized $SrTiO_3$-$SrCO_3$ (STO-SCO, with ~17 wt. % SCO), NiO/STO-SCO, Au-STO-SCO and Au-NiO/STO-SCO. While the preparation of NiO/STO-SCO was realized by wet impregnation (~0.3 wt. % NiO), the decoration of the previously mentioned catalysts (i.e., STO-SCO, NiO/STO-SCO) with Au was performed by photodeposition (~1 wt. % Au). The as prepared catalysts were assessed by complementary methods, namely ICP-OES, SEM-EDX, TEM, XRD, DRS, nitrogen sorption, DRS, Raman, EIS and PC. The CO_2 reduction activity of the samples was evaluated in a high-purity gas phase photoreactor system [3] in batch mode. Furthermore, the elucidation of CO_2 reduction mechanism was supported via in situ DRIFTS CO_2 adsorption experiments.

Results and discussion. The efficiency of impregnation and photodeposition was proven by ICP-OES. The XRD patterns confirmed the presence of cubic $SrTiO_3$ and orthorhombic $SrCO_3$ crystal phases in all of the studied samples. Furthermore, the plasmon resonance band situated at 540 nm offered a preliminary indication about the size of Au NPs in the case of all Au-modified samples, which was further proven by TEM. The preliminary results provided by EIS and PC measurements confirmed the improved charge separation and transfer efficiency in the case of Au-STO-SCO and NiO/STO-SCO in comparison to STO-SCO.

While the selective CH_4 formation was detected in the case of STO-SCO and NiO/STO-SCO catalysts, C_2H_6 was produced over Au-NiO/STO-SCO with >99% selectivity during the photocatalytic CO_2 reduction experiments. Furthermore, the photocatalytic production of H_2 was observed only in the case of the Au-STO-SCO sample. The adsorbed species on the surface of the catalysts were evaluated via in situ DRIFTS in the dark and under light irradiation (λ=320-700 nm). Considerable spectral differences were recorded in the case of Au-containing samples under light irradiation (*vs*. without irradiation), which may be correlated not only to their light harvesting capability but also to the thermal plasmonic effect of the Au NPs. The unraveling of possible causes (i.e., activation of adsorbed CO_2, light induced oxygen desorption, etc.) for spectral differences under *vs.* without irradiation is an ongoing work for all of the studied samples. Current research efforts aim at the investigation of possible synergistic effects between the special features provided by the components (i.e., oxygen vacancies in STO-SCO and surface plasmonic effect of Au NPs).

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Photocatalysts based on TiO_2 and activated carbon for the ethylene removal from air stream

A.M. Regadera-Macias, S. Morales-Torres, L. M. Pastrana-Martínez, F.J. Maldonado-Hódar

NanoTech – Nanomaterials and Sustainable Chemicals Technologies, Department of Inorganic Chemistry, Faculty of Science, University of Granada, Avda. Fuente Nueva, s/n, ES18071 Granada, Spain
**Corresponding Author's E-mail address (semoto@ugr.es)*

Keywords: Composites, adsorbents, photocatalysts, ethylene, perishable fruits.

Introduction. The removal of ethylene from the atmosphere of storage chambers for perishable fruits is a critical factor in the agro-food industry to avoid ripening and the consequent economic loss [1]. Ethylene can be removed by adsorption or oxidised to CO_2. In this work, composite materials based on biocarbons (ACs) and TiO_2 are developed to obtain a synergistic effect between adsorption and photocatalytic oxidation. The physicochemical properties and nanostructure of the materials are optimised by adjusting the proportions of the phases and the conditions of the hydrothermal synthesis (T, time, concentration of reactants) and their influence on the ethylene removal processes is analysed under different experimental conditions (ethylene concentration, UV or Vis radiation, contact time, etc.).

Experimental/methodology. ACs are previously prepared by physical activation in steam from olive stones. Carbon-TiO_2 composites were prepared in a ratio of 1:1 , 1:2 or 1:3 by hydrothermal deposition at 150 °C for 48 h in 8 or 12 M solutions of NaOH to fit the TiO_2 nanostructure. Finally, the obtained powders were pre-treated at 300 °C in air atmosphere and deeply characterized (TG, gas adsorption, XPS, XRD, UV-Vis diffuse reflectance). Adsorption / photocatalytic experiments were carried out using a mixture of C_2H_4/Air/H_2O with a C_2H_4 concentration of 50-1000 ppm and 50% of relative humidity (RH), using a medium-pressure mercury lamp (125 W, mod. 3010/PX0686) from Photochemical Reactors LTD., equipped with a glass water cooling jacket. The amounts of transformed C_2H_4 and formed CO_2, as unique reaction product observed, were monitored by GC (Shimadzu GC-2010 Plus) during the reaction time.

Results and discussion. ACs were microporous, while mesoporous TiO_2 nanorods or nanospheres were obtained depending on the synthesis conditions, mainly constituted by anatase or a mixture of anatase-brookite. ACs avoid the transformation into rutile of the nanoparticles. These TiO_2 nanostructures are also obtained inside the large cavities of ACs which confer a large micro/mesoporosity to the composites. The removal of ethylene by adsorption is mainly governed by the narrow microporosity of the samples, although can be favoured by the acidity of the surface (pH_{PZC}). The adsorptive performance of the samples decreases as the ethylene concentration in the flow, denoting the influence of the pore size distribution (activation degree) and the diffusion processes. It is noteworthy that all carbon-TiO_2 samples showed an enhanced absorption at wavelengths higher than 380 nm (visible range) in comparison with pure TiO_2, thus favouring also the photo-oxidation of ethylene. This process is selective to CO_2 and evidently, the activity of the samples is favoured using UV-Vis radiation regarding the near-UV-Vis one, and also by increasing the TiO_2 ratio in the composite up to 80% wt. The developed porosity of composites, their reduced band-gap and the fitted nanostructure and dispersion of the active TiO_2 phase improve their performance regarding pure fractions, confirming the synergetic effects between phases. The use of agricultural residues to produce the carbon phase and the activity of the composites under visible light, could favour the use of these type of materials in the development of filters and photoreactors, saving energy and resources in an environmental and circular economy concept.

Acknowledgments

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Innovative eco-friendly easily recoverable materials for olive mill wastewater treatment

M. G. Galloni[1,2,*], V. Nikonova[1], E. Falletta[1,2], C.L. Bianchi[1,2,*]

[1] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133, Milano, Italy.*
[2] *Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via Giusti 9, 50121, Firenze, Italy.*
[*] *melissa.galloni@unimi.it*

Keywords: easily recoverable photocatalysts; olive mill wastewaters; environmental remediation.

Introduction. Olive oil production, one of Europe's most flourishing agricultural industries, generates olive oil, pomace, and olive mill wastewaters (OMWW). These latter, composed of *ca.* 80-83 wt.% water, 2 wt.% inorganic matter, and *ca.* 15-18 wt.% organic compounds (i.e., polyphenols, phenols, and tannins), require proper disposal treatments. In this field, the development of efficient strategies is fundamental. Heterogeneous photocatalysis has emerged for its efficiency, sustainability, and integration potential in water purification systems. Here, innovative, sustainable and efficient photocatalysts design is the key point [1]. In this work, we present our preliminary results related to the development of eco-friendly, easily recoverable three components material (bismuth oxybromide supported onto Fe_3O_4-alginate spheres) for the treatment of polyphenols representatives of the OMWW fraction.

Experimental/methodology. Advanced, easily recoverable materials were fabricated by co-precipitating BiOBr onto alginate spheres containing a Fe_3O_4 core (Fig. 1a). Targeted physico-chemical characterizations were carried out to elucidate the samples properties. Gallic acid (GA) was selected as a model polyphenol: its abatement was monitored in the dark and under solar or visible light irradiation [2]. Preliminary abatement tests of gallic acid were also carried out on BiOBr powders.

Results and discussion. When BiOBr was supported onto alginate spheres with the Fe_3O_4 core, it was able to produce photocatalytic activity as if used in powder form. Fig. 1b depicts a SEM micrograph showing the BiOBr morphology between flower- and plate-like. Fig. 1c summarizes a results selection obtained for the GA abatement onto Fe_3O_4-alginate-BiOBr. In the dark region, the higher the catalyst amount, the higher was the GA abatement due to GA adsorption onto the catalyst surface, thanks to the ability of Bi centers to coordinate GA. After 180 min of irradiation, full GA photodegradation is reached for 5 g catalyst and *ca.* 95% for 1 g. The comparison of these results (green triangles) with those obtained only in the dark (dotted black line) confirmed that the material operates an explicit photocatalytic activity.
The encouraging results as well as the great advantage of the easy recovery currently move our research efforts towards the optimization of these eco-friendly photocatalysts for olive mill wastewater treatment.

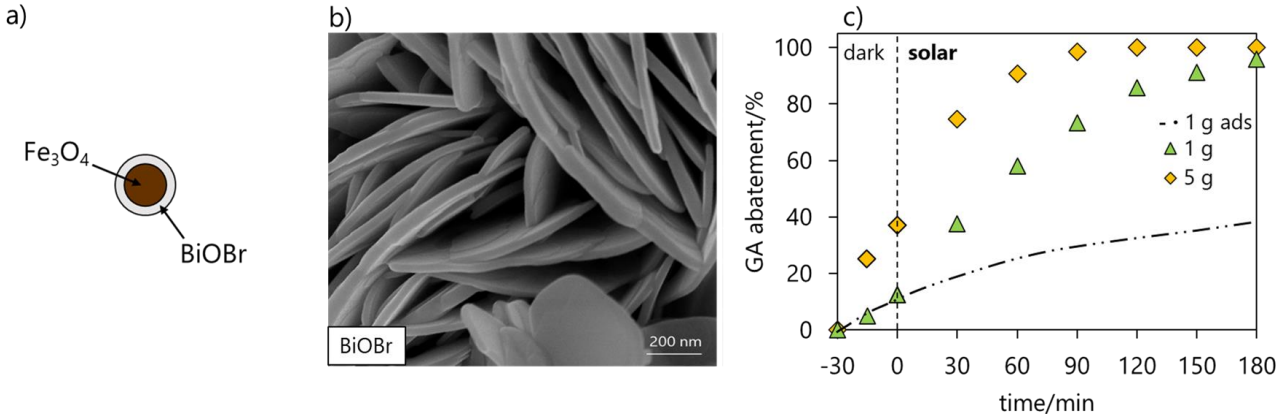

Fig.1: a) BiOBr-alginate-Fe_3O_4; b) SEM micrograph; c) GA abatement tests (10 ppm) under solar light (35 W/m^2).

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Photocatalytic Reduction of CO_2-to-CO using a CNQD·[Fe-p-TMA] Hybrid Assembly in Water

L. Mistry[1], L. Le-Quang[1], G. Masdeu[1], W. Björkman[1], H. Härelind[2*], M. Abrahamsson[1]

[1]Chemistry and Biochemistry, [2]Competence Centre for Catalysis, Dept. Chemistry and Chemical Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden
**hanna.harelind@chalmers.se*

Introduction.
The ever-increasing atmospheric CO_2 puts focus on the possibility to convert CO_2 into organic fuels or value-added products, preferably using environmentally benign methods. However, to break the stable carbon-oxygen double bonds calls for the use of electrochemical or catalytic routes to overcome the thermodynamic barrier [1]. Thus, utilizing sunlight in a photocatalytic approach to CO_2 reduction is an attractive solution, in particular systems that operate under relatively mild conditions and without additional energy requirements. In this work we present an efficient and selective water-soluble photocatalytic system with an iron-porphyrin catalyst electrostatically coupled to functionalized carbon nitride quantum dots (CNQDs) for the reduction of CO_2-to-CO, using visible light. The hybrid assembly shows excellent performance under mild conditions with high TON and selectivity around 96 % in water.

Experimental/methodology.
Existing literature protocols were used in the preparation of the iron porphyrin catalyst, [Fe-p-TMA]·Cl [2] and the CNQDs [3]. The photocatalytic experiments [4] were carried out in a Pyrex glass photoreactor coupled to a mass spectrometer continuously measuring gaseous products *in operando*. The visible light was generated using a Xenon lamp combined with a UV and an IR filter allowing for the transmission of only visible light (400 – 700 nm, ~55 mW cm^{-2} at 405 nm).

Results and discussion.
The photosensitizer-to-catalyst ratio was investigated by varying the concentration of [Fe-p-TMA] while keeping the CNQDs concentration constant. An optimal catalyst concentration of 1.0 µM was found, with a CO yield of ~200 µmol/h with high selectivity (~96 %, ~4 % H_2) for 10h irradiation, resulting in a TON_{CO} of ~10^5 or TOF_{CO} of ~12 s^{-1}. Increasing or decreasing the concentration of [Fe-p-TMA] resulted in a drop in CO formation. The mechanism for photo-induced CO_2 reduction using a sensitized iron-porphyrin catalyst is debated in literature [5,6]. Generally, it is agreed that the iron center is stepwise reduced to zero-valent, then forming an Fe-CO_2 adduct (Fe^{I}-CO_2^{-} or Fe^{II}-CO_2). The Fe-CO_2 is then protonated, forming H_2O and an Fe^{II}-CO intermediate. Photoexcitation of the QD and subsequent donation of a second electron results in cleavage of CO from the iron-porphyrin. In this work, we only observe the Fe^{II} and Fe^{I} states, *i.e.* no Fe^0 state. Thus, our results imply a mechanism with a CO formation route via a reversible $Fe^{II} \leftrightarrow Fe^{I}$ transformation induced by visible light irradiation of the CNDQ·[Fe-p-TMA] hybrid assembly in aqueous solution.

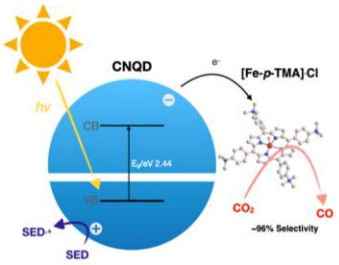

Figure 1. Illustration of the photocatalytic system (retrieved from [4]).

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Photocatalytic Oxidation in the Fine Chemical Industry

Werner Bonrath[1], Thomas Buchholz[2], Jonathan A. Medlock[1], Dragan Miladinov[2], Jan Schütz[1*], René T. Stemmler[1], Christof Sparr[2], Joël Wellauer[2]

[1]*DSM Nutritional Products Ltd., 4002 Basel, Switzerland*
[2]*Department of Chemistry, University of Basel, Switzerland*
[*]*jan.schuetz@dsm.com*

Introduction

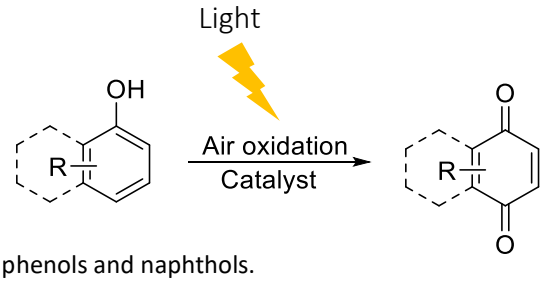
Photo-chemical processes are applied at DSM Nutritional Products since many years. The sigmatropic isomerization of 7-dehydrocholesterol to previtamin D_3 is carried out in a flow process under irradiation with ultraviolet light on industrial sclae. In the production of calcifediol (25-OH-vitamin D_3) a similar photo-chemical flow process is applied in the isomerization of 25-OH-7-dehydrocholestrol to calcifediol [1].

Experimental/methodology

A continuous flow photoreactor using visible light from high intensity LEDs and if required air overpressure was applied in the presented studies. The reactor design permits the use of low photocatalyst loadings to promote singlet oxygen generation and allows precisely controllable principal process parameters.

Results and discussion

In several research and development projects at DSM Nutritional Products photo-chemical and photo-catalytical processes were studied. Important examples are the *E*/*Z*-isomerization of 3-methyl-pent-3-enynes, compounds used in the manufacture of vitamin A acetate and astaxanthin and the E/Z-isomerization of vitamin A acetate (the final product is (all-*E*)-vitamin A acetate) [2]. Another examples is the [2+2+2] cycloaddition of alkynes and nitriles to a precursor in the synthesis of vitamin B_6 [3]. The oxidation of phenols and naphthols to their corresponding quinones was studied under photo-catalytic flow conditions (Scheme 1) [4]. Some of these quinones are intermediates in the manufacture of vitamin E and K_3. The method allows to oxidize phenols with high selectivity under mild reaction conditions using visible light. The reactor design permits low photosensitizer loadings to generate singlet oxygen. This efficient phenol oxidation might become a valuable part in a sustainable approach to vitamin E and related compounds.



Scheme 1. Photocatalytic oxidation of phenols and naphthols.

Herein selected aspects of industrial applications of photo-catalytical processes will be discussed.

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Simultaneous coupling of photocatalysis and Fenton-based processes: an efficient strategy for water treatment?

S. Gowrisankaran[1], M. Motola[1], H. Makarov[2], G. Mailhot[3], M. Brigante[3], O. Monfort[1*]

[1]*Comenius University Bratislava, Faculty of Natural Sciences, Bratislava, Slovakia*
[2]*Comenius University Bratislava, Faculty of Physics Mathematics and Informatics, Bratislava, Slovakia*
[3]*Université Clermont Auvergne, CNRS, Institut de Chimie de Clermont-Ferrand, Clermont-Ferrand, France*
[*]*monfort1@uniba.sk*

Keywords: TiO_2 nanotube, iron, photocatalysis, Fenton, caffeine, water

Introduction. Photocatalysis and Fenton-based processes are well known advanced oxidation processes (AOPs), especially for the degradation of organic pollutants in water [1]. Titania (TiO_2) is one of the most popular photocatalyst which is interesting in the form of nanomaterials due their unique properties, like the high charge carriers transport in highly-ordered self-organized TiO_2 nanotube layers [2]. Fenton reagents including iron species and hydrogen peroxide are promising since they are low-cost along with high availability [3]. However, both these AOPs exhibit drawbacks (electron-hole pairs recombination, iron sludge production, etc.), that can be potentially limited by coupling TiO_2 and Fe within a single material. Therefore, this conference presentation aims first, to characterize the physico-chemical properties of synthezied Fe surface-modified TiO_2 nanotube layers (Fe-TiO_2) and then, to assess the contribution of each identified AOP triggered by Fe-TiO_2. To this end, their simultaneous coupling is discussed by investigating the performance of Fe-TiO_2 for the degradation of caffeine, a top pharmaceutical contaminant, in water.

Experimental. Fe-TiO_2 is prepared by electrochemical anodization of titanium foil (1.5 cm x 1.5 cm) followed by surface modification using spin-coating of Fe(III) precursor solution at different concentrations. The different Fe-TiO_2 are annealed at 450 °C for 2 h in air, and subsequently characterized by XRD, DRS, SEM, EDX and UPS. The generation of hydroxyl radicals (HO•) is analyzed by fluorescence spectroscopy (using 7-hydroxycoumarina as probe) while iron leaching is investigated by UV-VIS spectrocopy (using ferrozine complexation). The degradation of caffeine (20 ppm, pH = 3) by Fe-TiO_2 is performed in a batch photoreactor equipped of UVA light (1.3 mW/cm²) with the addition of 500 µM H_2O_2. The degradation extents and mechanism are investigated by HPLC and LC-MS, respectively.

Results and discussion. To fundamentally understand the coupling mechanism between photocatalysis and Fenton, Fe-TiO_2 with intermediate surface-concentration of iron (100 µM) is the optimal strategy since, in the extremes of the series (10 µM and 10 mM), the degradation of caffeine is governed exclusively by photocatalysis and Fenton-based processes, respectively. In the optimized Fe-TiO_2, the contribution of H_2O_2 photolysis, photocatalysis and Fenton-based processes in the degradation of caffeine (67% after 3 h) has been evaluated 4%, 23.5% and 39.5%, respectively. It is worth noting the Fenton contribution is due to the iron leaching (2.3 µM). HO• have been identified as the main active species during the degradation of caffeine. The main degradation by-products have been identified, thus leading to the proposal of hydroxylation, N-demethylation and imidazole ring opening as plausible mechanisms. To conclude, the strategy of coupling photocatalysis and Fenton-based processes is promising since it introduces the concept of photochemical versatility. Such an innovative approach could potentially reduce the cost of water treatment by introducing a synergy between the processes.

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ZnO/ZnS heterostructure photocatalyst for complete removal of azo dyes and fluoroquinolone antibiotics in wastewater

Tammanoon Chankhanittha. Suwat Nanan*

[1]*Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002 Thailand*
**Corresponding Author's E-mail address:suwatna@kku.ac.th*

Keywords: ZnO/ZnS photocatalyst, Azo dyes, Antibiotics, Wastewater treatment, Environmental Protection

Introduction. The presence dyes and antibiotics in high concentrations found in natural water for long times resulted in carcinogenesis, mutagenesis, and respiratory toxicity in addition to other various side effects. Therefore, the complete removal of the organic pollutants including dyes and antibiotics is urgently needed. Various conventional treatment routes including adsorption face some drawbacks such as low efficiency, high cost, and creation of secondary pollutants. Alternatively, semiconducting photocatalytic method is a promising technique for purification of water without generation of any harmful product [1]. Photogenerated electron-hole recombination is an important factor limiting the efficiency of the photocatalyst. Therefore, the development of heterojunction photocatalysts has become an inevitable trend. Recently, the ZnO/ZnS heterostructures have been attracting significant interests from their predominant properties to combine ZnO and ZnS with lower photoexcitation threshold than individual components and decrease the recombination rate of electron-hole pairs by their physically separated band gap [2].

Experimental/methodology. The ZnO/ZnS heterojunction was prepared by thermal treatment of hydrothermally grown ZnS in air at various temperatures. The evolution of the structural and morphological transformation was investigated. The photocatalytic performance of the prepared ZnO/ZnS photocatalyst toward degradation of Reactive red 141 (RR141) and Congo red (CR) dyes was investigated. In addition, the photoactivity of the prepared photocatalyst toward degradation of two fluoroquinolone antibiotics namely ofloxacin (OFL) and norfloxacin (NOR) was also examined. Both simulated UV light (135 W) and natural sunlight were used. The exact concentration of the remaining pollutant was determined by spectrophotometric method.

Results and discussion. The ZnS-500 (ZnS calcined at 500 °C) contains the ZnO/ZnS heterojunction showing the highest photodegradation activity toward degradation of azo dyes (RR141, CR) and antibiotics (OFL, NOR) under both UV light and natural sunlight irradiation. The combination of ZnS and ZnO is the key factor regarding the enhancement of the photocatalytic performance by suppressing the recombination of photogenerated electron-hole pairs. The photodegradation of the pollutant follows the first-order kinetic model. The excellent recycling ability of the ZnO/ZnS photocatalyst was confirmed after five cycles of use. The prepared photocatalyst also shows good structural stability with the similar morphology after photocatalytic study. This work demonstrates that the ZnO/ZnS heterojunction photocatalyst has a high potential for detoxification of harmful organic pollutants inclouding dyes and antibiotics from the aqueous solution.

Acknowledgments
We would like to thank the fund supported by Materials Chemistry Research Center (MCRC) and Khon kaen University.

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Synthesis and Characterization of Ceria-Silica Nanocomposites for CO_2 Photocatalytic Reduction

Yi-Ru Zhao, Po-Chih Tsao, I-Hsiang Tseng*

Department of Chemical Engineering, Feng Chia University, Taichung, Taiwan
**ihtseng@fcu.edu.tw*

Keywords: CeO_2, SiO_2, CO_2, photocatalysis

Introduction.

The facile formation of oxygen vacancy and the redox capability of Ce^{3+}/Ce^{4+} make ceria (CeO_2) a popular adsorbent or catalyst material [1-2]. The difference in the morphology of CeO_2 leads to various amounts of surface defects on CeO_2 [3]. In this work, process parameters were carefully tuned to obtain CeO_2 with different nanostructures (cube or rod). The combination of nanosized SiO_2 reduced the crystallinity of CeO_2 and created more defect sites on CeO_2.

Experimental/methodology.

In this work, the modified precipitation method combined with hydrothermal process was applied to synthesize CeO_2 nanoparticles with rod or cube crystallinity. For CeO_2-SiO_2 samples, various amounts of commercial SiO_2 nanoparticles were added during the above fabrication process. The precursor of CeO_2 was $Ce(NO_3)_3 \cdot 6H_2O$.

Results and discussion.

TEM images (Fig. 1) and XRD patterns (Fig. 2) confirm the morphology and crystallinity of CeO_2. The absorption edge of c-CeO_2 is at 430 nm, corresponding to the band gap of 3.10 eV. Red shift of the absorption edge is observed from r-CeO_2, that is 460 nm (2.85 eV), due to more oxygen vacancies. The addition of SiO_2 does not affect the optical property. Increasing NaOH concentration from 6M to 9M during precipitaion process improves the crystallinity of rods as well as enhances the production of methoanol (MeOH). In addition to MeOH, carbon monoxide and H_2 are detected from the photocatalytic reaction of CO_2 and H_2O. XPS and Raman spectra reveal that rod CeO_2 and samples containing SiO_2 exhibit more defects. EPR spectra confirm the presence of spin adducts (DMPO-OH), indicating the production of hydroxyl radicals from irradiated samples suspending in the spin-trap reagent (DMPO). The roles of oxygen vacancy and intermediate radicals in CO_2 activation and conversion are investigated in this work.

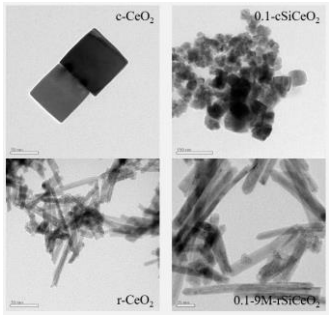

Figure 1. TEM images of CeO_2 and CeO_2-SiO_2.

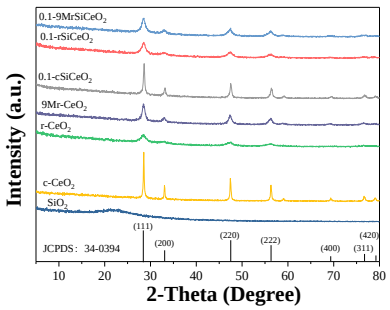

Figure 2. XRD patterns of SiO_2, CeO_2 and CeO_2-SiO_2.

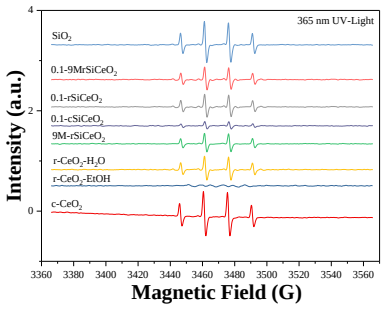

Figure 3. EPR spectra of samples in DMPO solution under UV illumination.

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This work was supported by National Science and Technology Council of Taiwan under the project number of MOST 109-2221-E-035-019-MY3.

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Photocatalytic oxidation of isopropanol in the presence of organic coatings containing TiO_2 nanoparticles

Sara Golbarg[1], Kim Dam-Johansen[1] and Jakob M. Christensen[1*]

[1]*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads 228A, 2800 Kgs. Lyngby (Denmark)*
[*]*jmc@kt.dtu.dk*

Keywords: Photocatalysis, Metal oxide catalysis, Oxidation.

Introduction. Photocatalytic oxidation of pollutants in the air has been the subject of substantial research and is considered to be a promising strategy to improve air quality [1]. In practical applications of this technology the photocatalyst will often be incorporated as a pigment into a paint formulation [2][3]. Hence, an understanding of how the photocatalyst is most optimally incorporated into the coating and which factors that impact performance is of vital understanding for the practical use of photocatalytic processes. Among volatile organic compounds (VOCs) alcohols are at the central class and due to their widely use they are responsible for the poor air quality. The photocatalytic oxidation of isopropanol at the presence of a photocatalyst powder has been investigated extensively [4]. However, the application of photocatalytic paints for this purpose still requires research since there are many parameters affecting the performance of this type of paint. For this purpose experiments were performed using coatings containing TiO_2, primarily in the form of nanoparticles, as the photocatalytic component. For the experiments that involve the study of the effects from multiple factors, factorial experiment design can be a useful tool and was used in these studies. In this work, the effect of three primary factors: the content of solid binder, the photocatalyst mass and irradiation intensity on three responses: the conversion of isopropanol, CO_2 formation from oxidation and the pseudo-first order rate constant after 3 hours of reaction, has been investigated.

Experimental/methodology. Simplified organic coating formulations were prepared on a flexible plastic substrate through dispersion of commercial TiO_2 nanoparticles in a waterborne acrylic using an ultrasonic processor. A tubular glass cell was chosen as a lab scale photoreactor which was equipped with two KBr windows for simultaneous IR analysis in transmission mode. An Arcadia 80 W D3 UV lamp was used as the source of irradiation. The radiation intensity was adjusted by changing the distance between the lamp and the photoreactor. Isopropanol was introduced into the photoreactor by injection of 1 µL The Design Expert software was used to perform factorial experiment design.

Results and discussion. The result show that the photocatalyst mass in the coating doesn't have a significant effect on across a wide concentration range. This shows that in a real coating system the photocatalyst particles can easily shield each other and negate the effect of larger concentrations. On the other hand the solid binder content and irradiation intensity had a significant impact on the isopropanol conversion. Decreased solid binder content, enhance the conversion of isopropanol and formation of CO_2. It can be concluded that a larger content of binder in the coating sample shields the photocatalyst and decreases the number of active sites and consequently decreases the generation of active radicals. As expected an increased irradiance intensity also raises the conversion. The results illustrate that the catalytic activity of the coating relies on the unshielded photoatalytic particles at the external surface of the coating and that methods for achieving the appropriate positioning of the catalyst within a coating medium are essential for the practical applications of photocatalysis.

Acknowledgments

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Synthesis of WO_3-Ag-AgCl films for application in continuous photocatalytic microreactors

P. H. Palharim[1,2*], T. Bürgi[2], A. C. S. C. Teixeira[1]

[1]*University of São Paulo, São Paulo, Brazil*
[2]*University of Geneva, Geneva, Switzerland*
[*]*ppalharim@usp.br*

Introduction. As new environmental pollutants cannot be adequately removed by conventional water treatment techniques, they pose a significant risk to the aquatic ecosystem [1,2]. Therefore, advanced oxidative processes have shown promising results for wastewater treatment, particularly heterogeneous photocatalysis. Among commonly studied semiconductors, WO_3 is a material with interesting properties: its narrow band gap (2.5-2.8 eV) makes it active in the broad UV-visible range. Silver-based materials (Ag_2S, Ag_2WO_4, AgCl etc.) can be coupled to WO_3 to increase its photocatalytic activity at a low cost, while extending its absorption range into the visible spectrum and reduzing charge recombination [3,4].

The type of reactor is also important; although batch reactors are commonly used to evaluate the efficiency of these materials, their use is mainly restricted to laboratory investigations. Continuous microreactors allow an initial evaluation of different photocatalysts in reduced scale, and allow the study of scale-up [5]. Additionally, among the various charactterization strategies, vibrational spectroscopy is a valuable technique to provide information about adsorbate layers and in situ investigations of heterogeneous catalysis. In this context, this work aims to synthesize WO_3 films coupled with Ag-AgCl, evaluate their photocatalytic performances in microreactors under simulated sunlight using acetaminophen (ACT) as a model contaminant, and evaluate in situ spectroscopy analyses with tbe best materials.

Experimental/methodology. All materials were synthesized by the ultrasonic nebulization-pyrolysis/photoreduction method. A central composite experimental design was used to optimize the volume of solution containing the WO_3 precursor and the concentrations of $AgNO_3$ and NaCl deposited on the substrate. To evaluate the photocatalytic activity, the films were placed on a 3D-printed microreactor, subsequently sealed. A 5-mg L^{-1} solution of ACT was fed to the reactor and the experiments were carried out with a HgI_2 lamp. Samples were collected over time and analyzed by HPLC using a C18 column and UV-vis detector. For the spectroscopic experiments, the catalyst was deposited onto an internal reflection element, which was placed in a flow-through cell mounted on an attachement for ATR (attenuated total reflection) measurements inside the sample compartment of a FTIR spectrometer.

Results and discussion. According to the central composite experimental design, the AgCl concentration is the most significant variable in relation to ACT removal, mainly after prolonged use of the material; while the volume of nebulized liquid containing the WO_3 precursor did not significantly affect ACT removal. The best material exhibit cracked plates and deformed nearly spherical particles, referred to as WO_3 particles, covered by small clustered spherical particles, identified as AgCl. Premilinarly in situ ATR analyses show that prolonged time of irradiation resulted in changes especially in the C-N-H and C=C chemical bonds. These results indicate that the heterojunction formed between WO_3 and AgCl may have resulted in a material with high photocatalytic activity under simulated sunlight.

Acknowledgments
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Visible-light photocatalytic activity screening of reduced TiO_2 in batch and flow: A sustainability analysis

A. Roibu[1*], R. Udroiu[2], L. Andronic[1]

[1]*Transilvania University of Brașov, Department of Product Design, Mechatronics and Environment, Brașov, Romania*

[2]*Transilvania University of Brașov, Department of Manufacturing Engineering, Brașov, Romania*

[*]*Corresponding author:anca.roibu@unitbv*

Introduction.

In semiconductor photocatalysis for water treatment, TiO_2 has become the benchmark semiconductor material [1]. However, the excitation wavelength of TiO_2 falls in the UV region which represents only 5% of the solar radiation.[2] The reduced TiO_2 shows light absorption commonly across the entire visible spectrum until near-infrared due to the introduction of Ti^{3+} and oxygen vacancies and is characterized by superior photocatalytic activity to pristine TiO_2 when irradiated with visible light.[3] Conventionally, the investigation of photocatalytic activity is performed in batch reactors, which are inexpensive and easy to operate, however, they predominantly require several hours of irradiation for each investigated material/condition. Contrary, photo microreactors are characterized by full pollutant degradation in less than 15 minutes, and when coupled with on-line analysis allow continuous monitorization and automation.[4] Despite these advantages, the use of continuous reactors in photocatalyst testing for water treatment is limited. In the context of intensified research for identifying efficient photocatalysts and collective effort for rational use of resources, there is a lack of sustainability assessment of the two screening methods. Consequently, this work aims (i) to investigate the effects of reduced TiO_2 synthesis and operational conditions on photocatalytic activity under visible light irradiation of batch and flow reactors and (ii) to compare the two screening methods by their testing throughput, consumption of reagents and electrical energy, and the reproducibility of acquired data.

Experimental/methodology.

The synthesis of defective TiO_2 is performed by the chemical reduction of TiO_2 with $NaBH_4$. A set of materials with tailored properties is prepared by varying the temperature and reduction time and is characterized by N_2 sorption, X-ray diffraction, Diffuse reflectance UV-vis spectroscopy, and X-ray photoelectron spectroscopy. The photocatalytic activity of the reduced TiO_2-based materials is tested in the degradation of phenol and imidacloprid at various operational conditions (e.g., catalyst loading, pH) using powdered materials in batch photoreactors and immobilized photocatalytic films integrated in microreactors. The flow microreactor is manufactured by 3D printing and allows the simple replacement of the photocatalytic film. The photoreactors are illuminated by in-house built LED light sources with emission at 394 nm, 467 nm, 520 nm, and 635 nm.

Results and discussion.

By varying the time and reduction temperature, colored TiO_2-based materials are obtained which are characterized by a 2-fold increase in the specific surface area and a decrease of the band-gap energy from 3.2 eV to 1.4 eV. Next, the photocatalytic activity of the synthesized materials will be investigated in batch and in flow. Finally, the sustainability of the screening methodologies will be assessed. The findings of this study are important for developing automatic screening and optimization platforms to accelerate the process of designing more efficient photocatalysts driven by visible light.

Acknowledgments

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Graphitic Carbon Nitride Thin Films for Visible Light Pollutant Degradation in Photo-microreactor

P. Stavárek[1*], P. Klusoň[1], D. Schimon[1], P. Dzik[2], T. Homola[3]

[1]*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 2/135, 165 02 Prague, Czech Republic*

[2]*Institute of Physical and Applied Chemistry, Faculty of Chemistry, Brno University of Technology, Purkyňova 464/118, Královo Pole, 612 00 Brno, Czech Republic*

[3]*R&D Centre for Plasma and Nanotechnology Surface Modifications, Faculty of Science, Masaryk University, Kotlářská 267/2, 611 37 Brno, Czech Republic*

[*]*Corresponding Author's E-mail address: stavarek@icpf.cas.cz*

Keywords: graphitic carbon nitride, photocatalytic film, photo microreactor, pollutant degradation

Introduction

Graphitic carbon nitride (g-C_3N_4) is a metal-free photocatalyst which has recently attracted significant interest of many researchers. Thanks to its beneficial physical, chemical and electronic properties it has been applied in photo and electrocatalysis, for pollutants degradadion, for water splitting, in heterogeneous catalysis and meny others. The band gap of g-C_3N_4 (2.7 eV) is lower than for TiO_2 (3.2 eV), and and therefore it can potentially offer excellent light harvesting capabilities even in the range of visible solar light spectrum. In this contribution we focuse on development of g-C_3N_4 thin films and testing for pollutant photodegradation using a photo-microreactor with a slit geometry.

Experimental/methodology

In this work, the g-C_3N_4 was synthesized from supramolecular complex of melamine and cyanuric acid that was calcinated at 550°C to provide g-C_3N_4 of high photocatalytic activity, see [1] for details. The thin films of g-C_3N_4 were prepared from mixture of ball-milled g-C_3N_4 and a binder. The prepared thin films of average thickness 27 µm were subjected to surface modification by plasma treatment to provide excellent hydrophilic properties. The resulting photocatalytic films were examined in a microphotoreactor with a slit geometry and compared to conventional slurry tests in a batch photoreactor. Degradation of three selected antibiotics emerging as waste water pollutants was performed. The degradation products were analyzed by HPLC-MS and possible degradation pahts are drawn.

Results and discussion

The photocatalytic activity of g-C_3N_4 to catalyse photodegradation of Tetracycline as one of the three chosen antibiotics is shown in the Figure 1. The conversion of Tetracycline reached 87% after 75 min; the photolysis of TC was negligible. Degradation of TC in the photo-microreactor with a thin layer of g-C3N4 showed about 175x higher specific kinetic constant compared to the batch reactor (k^* increased from 0.05 to 8.58 [$min^{-1}cm^{-2}g_{(g\text{-}C3N4)}^{-1}$]), indicating a vast improvement in the photodegradation process efficiency. The thin film photodegradation performance with with differrent polutants will be shown and discussed.

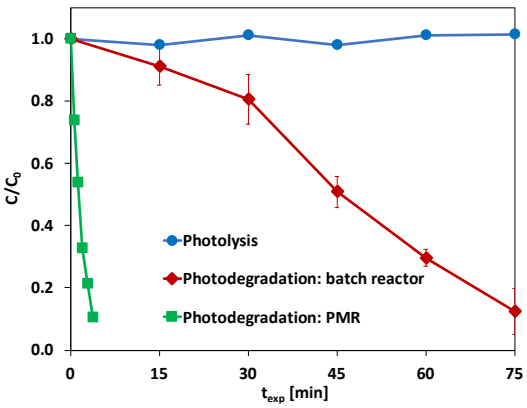

Figure 1 Tetracycline photodegradation over g-C_3N_4 in a batch reactor and photo-microreactor

Acknowledgments

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Photocatalytic H_2 Generation on TiO_2-based Catalysts and the Effect of the Reaction set-up Configuration on the Photocatalytic Effiency

S. Y. Toledo-Camacho[1*], K. Wenderich[2], G. Mul[2], S. Contreras[1], F. Medina[1]. [1]*Departament d'Enginyeria Química, Universitat Rovira i Virgili, Tarragona, Spain.* [3] *Photocatalytic Synthesis Group, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands. *sandrayurani.toledo@urv.cat*

Keywords: Photocatalysis, Hydrogen, TiO_2, Photoreforming, Co-catalysts, Quantum effciency

Introduction.

Our current wasteful lifestyle forces scientists to take up the challenge to develop more efficient materials to utilize the energy of renewable sources. Since Fujishima and Honda (1972), the H_2 photogeneration on semiconducting materials became a capable technology to produce other fuel sources rather than fossil fuels, but today, non-conventional methods are still not mature enough and inefficient [1]. In this work, we investigate the effect of different co-catalysts and the reaction set-up configuration on the activity of TiO_2 (commercial TiO_2 P25) and TiO_2 nanotubes (NT) for H_2 generation by photoreforming or water-methanol mixtures (50 vol.%).

Experimental/methodology.

P25-WO_3 and NT-WO_3 supports were synthesized according to reference [2]. The metal (Pd or Pt) was incorporated by photodeposition and Cu by wetness impregnation. The three H_2 set up under study were: (i) simulated solar light $(SSL)_{300\text{ - }800\text{ nm}}$, (ii) $UVA_{300\text{ - }400\text{ nm}}$ and (iii) small scale (SS) system, HP Hg $lamp_{280\text{ - }700\text{ nm}}$ [3].

Results and discussion.

In Figure 1 it is observed that Pd/P25 shows the highest H_2 evolution in all three reaction systems, where in SS- and SSL-system, Pd/P25 has the highest activity. Pd/P25-WO_3 presents same decreasing order, however, its activity is reduced compared to Pd/P25. For Pd/NT-WO_3, though it shows higher activity than Pd/P25-WO_3, its H_2 evolution is also importantly depleted compared to Pd/P25. Similar outcomes were found for the catalysts containing Pt and WO_3. Probably, the interaction between the metal (Pd or Pt) and WO_3 nanoparticles promotes byproducts adsorption on the catalyst, blocking the pathway towards H_2 [3]. When P25 is loaded with Cu and Pd, the catalytic activity also undergoes a decreasing. This negative activity exposes the absence of any synergy effect between both co-catalysts [4]. Still, in the SSL-system, Pd/P25-Cu was more active than all the catalysts containing WO_3, but, interestingly, its performance in the SS-system was the worst. In addition, Figure 1 shows the effect of the reaction set-up configuration on the final reading for H_2 evolution, under normalized conditions by the photon flux corresponding only to UV light (300 - 400 nm) ($I_{300\text{-}400\text{ nm}}$: $2.99\text{x}10^{-4}$ for SSL-, $8.33\text{x}10^{-5}$ for UVA- and $3.50\text{x}10^{-5}$ Einstein/min for SS-system). H_2 evolution per visible photon flux is also presented. The catalytic activity in the SS-system is fairly the highest, though, interestingly, its total φ (%) is closely similar or even lower than in UVA- and SSL-system. It reflects in the SS set-up there is a more effiencient interacion between catalyst and the inferior number of photon (light intensity) incoming to the reactor, whose small reactor into an enclosed chamber with an optical fiber allows a concentrated beam of photons. In the UVA- vs. SSL-system the vertical glass reactor irradiated with four elongated lamps around it probably favoured a better photon absorption than on a wider shape borosilicate reactor with irradiation on top, respectively.

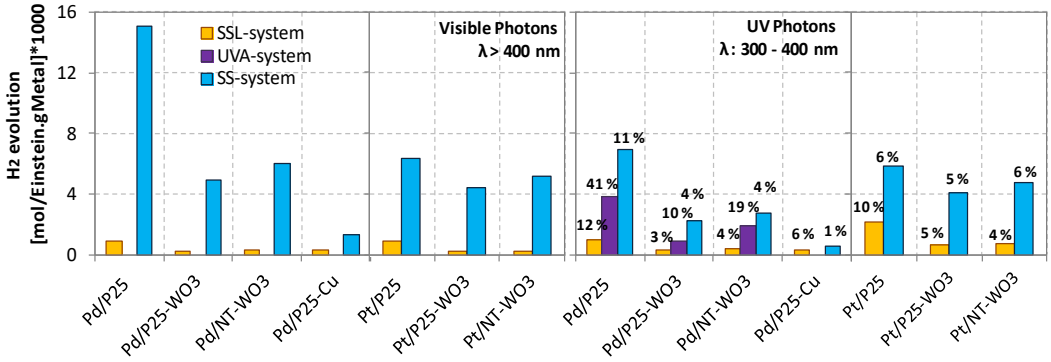

Figure 1. Photocatalytic H_2 evolution and Quantum Effiency, φ (%) in three different reaction set-up.

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Decabromodiphenyl ether photo-debromination via halogen bond activation on sulfur vacancies enriched zinc indium sulfides

Xueqing Jin[1], Chunyan Sun[1], Zhixin Yu[2], Qi Shen[1*]

[1]*Institute of New Energy, School of Chemistry and Chemical Engineering, Shaoxing University, Zhejiang Shaoxing 312000, China*

[2]*Department of Energy and Petroleum Engineering, University of Stavanger, Stavanger 4036, Norway*

[*]*shenqi@usx.edu.cn*

Keywords: Halogen bond activation; Sulfur vacancy; Polybrominated diphenyl ethers; Photocatalysis

As a class of halogenated flame retardants, polybrominated diphenyl ethers (PBDEs) are widely used in electrical products, furniture and textiles. Recently, as persistent organic pollutants, different levels of PBDEs have been detected in the atmosphere, soil, water and other environmental media. The environmental persistence of PBDEs has been shown to originate primarily from bromine atoms. Therefore, the activation of C-Br bond in PBDEs is particularly important for their debromination as well as for weakening environmental oxidation resistance.In this work, halogen bond targeted photocatalytic interface has been designed to activate C-Br bond, thereby improving the debromination efficiency of PBDEs photodegradation effectively.

Zinc indium sulfides $Zn_xIn_2S_{x+3}$ (x = 1, 2 and 3) with different sulfur vacancies concentration were constructed by a simple solvothermal method to achieve BDE209 debromination under irradiation. Under both UV (λ > 360 nm) and visible light (λ > 420 nm) irradiation, $ZnIn_2S_4$ has the most outstanding degradation ability to BDE209 (Figure 1a), attributing to its surface abundant sulfur vacancies. The introduction of sulfur vacancies can narrow the forbidden band of photocatalysts, thereby increasing their absorption and utilization of light. More importantly, the sulfur vacancies serve as active sites to facilitate the adsorption and activation of C-Br of BDE209. In addition, product analysis indicated that the removal of the first bromine atom of BDE209 on the sulfur vacancies was a *meta*-selective debromination process, which was the same as the debromination behavior on the oxygen vacancies (Figure 1b). Interestingly, the selectivity of meta-debromination on sulfur vacancies is as high as 70%, superior to that on oxygen vacancies. This is attributed to the larger vacancy space of the sulfur atom to accommodate the bromine atoms in BDE209, which helps to stabilize stabilization of the *meta*-bromine atomic adsorption configuration of BDE209 on sulfur vacancies. Meanwhile, the intermediate configuration is further stabilized under the assistance of the S···Br halogen bond by retained sulfur atom at the catalytic interface. This work sheds light on the great potential of sulfur vacancies in photocatalytic treatment of halogenated flame retardant pollutants.

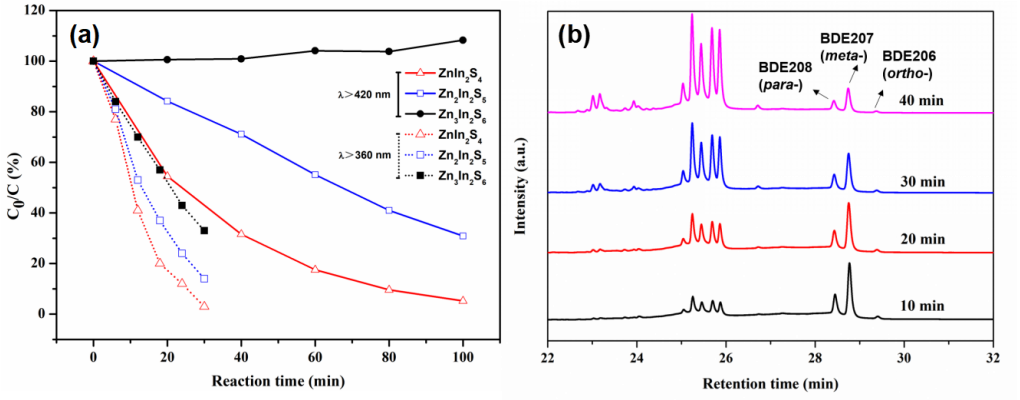

Figure 1 (a) Comparison of photocatalytic degradation of BDE209 over $ZnIn_2S_4$, $Zn2In_2S_5$ and $Zn_3In_2S_6$ in N_2-blanketed methanol system; (b) GC-μECD chromatograms of degradation products of BDE209 for $ZnIn_2S_4$ at 10, 20, 30 and 40 min.

Acknowledgments

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Enhancement of hydrogen production using gold coordination compounds anchored on TiO_2 hybrid photocatalysts

A. Agrelo[1], L. Soler[1*], E. Martínez[2], I. Angurell[2], L. Rodríguez[2], J. Llorca[1*]

[1] *Institute of Energy Technologies and Department of Chemical Engineering, Universitat Politècnica de Catalunya (UPC), Spain*

[2] *Departament de Química Inorgànica i Orgànica, Secció Química Inorgànica, Universitat de Barcelona, Spain*

[*] *Corresponding Author's E-mail: lluis.soler.turu@upc.edu; jordi.llorca@upc.edu*

Keywords: heterogeneous photocatalysis, continuous flow reactor, Au complexes, titania, surface plasmon resonance

Introduction. One of the most promising approaches to use water and organic compounds as sources of hydrogen is through solar photocatalytic reactions. Despite the simple nature of the idea and its potential technical viability, the currently available photocatalysts show too low hydrogen production yields in the range of sunlight. In order to increase the effectiveness of the light-to-hydrogen conversion, there is a substantial interest in creating new photocatalysts with improved light absorption [1-4]. In this study, various hybrid gold(I)/gold(0) complexes were loaded over titania and used as photocatalysts for hydrogen production, more specifically for ethanol dehydrogenation. The impact of the preparation technique [5] on the photocatalytic activity under UV and visible light was also analyzed.

Experimental. A conventional impregnation method and a mechanochemical method were used to anchor gold complex co-catalysts on TiO_2 with a mass loadings of 1%. An additional set of samples was prepared by incipient wetness impregnation with a co-catalyst load of 0.25% wt. Au, in order to analyze the effect of the different ligands of the complexes. Photocatalytic experiments were carried out at room temperature under atmospheric conditions in a continuous gas flow photoreactor (GHSV = 5600 h^{-1}). All the samples were characterized before and after reaction using UV-Vis spectroscopy, RAMAN spectroscopy, X-ray diffraction, XPS, and TPR.

Results and discussion. Photocatalytic experiments show an improvement of the activity of all samples compared to pure titanium dioxide (P90) under UV irradiation, as well as hydrogen generation capability under visible light. Generally, samples prepared by the mechanochemical method show lower photocatalytic activity than those prepared by impregnation, which is a good point in favour of the conventional method. The samples with Au(I)-based co-catalysts show a reaction profile in which the hydrogen production rate increases constantly until it stabilizes, which could be indicative of a possible rearrangement of gold from Au(I) to Au(0). This is confirmed by the UV-Vis spectra of the samples after reaction, as they show an absorption band corresponding to gold plasmon. In the case of the photocatalyst with Au(0)-based complexes, the reaction profile shows a decrease in hydrogen production prior to stabilisation, which is related to a reorganisation of the gold in the form of agglomeration of nanoparticles. The impregnated samples with a complex load of 1%, showed improvements in the activity, ranging from 18% to 74%, when irradiating with UV light compared to an Au/TiO_2 reference sample with a gold content of 1% by weight. A set of samples with the same amount of gold was prepared (0.25% wt.) in order to analyze a possible influence of the different ligands.

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Ag nanoparticle doped ZnO thin films: Preparation and applications in photocatalysis and antibacterial applications

A. H. Haritha[1,2*], Z. Neščáková[1], A. Durán[2], D. Galusek[1,3], J. J. Velázquez[1], Y. Castro[2]

[1]*FunGlass, Alexander Dubček University of Trenčín, Trenčín, Slovakia,*
[2]*Instituto de Cerámica y Vidrio (CSIC), Madrid, Spain*
[3]*Joint Glass Centre of the IIC SAS, TnUAD,nd FChPT STU, Trenčín, Slovakia*
[*]*Corresponding Author's E-mail address: haritha.haridasan@tnuni.sk*

Keywords: ZnO thin films, Ag nanoparticles, photocatalytisis, antibacterial, sol-gel dip-coating.

Introduction

ZnO thin films doped with Ag nanoparticles (AgNPs) can be promising candidates for photocatalytic and antibacterial applications [1] due to their improved electron movility and decrease of the charge trapping compared to pure ZnO. The preparation of AgNP doped ZnO thin films involves the preparation and incorporation of Ag nanoparticles suspensions into a ZnO sol, which can be achieved through various synthesis methods, including sol-gel, sputtering, and hydrothermal methods. In general, the sol-gel method is a simple and cost-effective approach for the preparation of Ag-doped ZnO thin films [2].
Thus, in this work, we explored the most appropiate way to synthesize the suspensions of Ag nanoparticles and to incorporate them to ZnO sols. The deposition of Ag-doped Zn thin films was also studied by dip-coating together with the characterization of photocatalytic and antibacterial performance of the coatings.

Experimental/methodology: The Ag nanoparticles suspensions were synthesized using a chemical reduction method by adding silver nitrate to a solution of ethanol and polyvinypyrolidine. AgNPs doped ZnO was prepared by mixing zinc acetate dihydrate, ethanol, and diethanolamine and adding the previously prepared Ag nanoparticles suspension. The Ag-doped ZnO sol-gel solution was used for dip-coating glass substrates and Si wafer, which was then dried for 1 h at 80 °C and calcined at 450 °C for 1 h to obtain AgNP-doped ZnO thin film. The resulting thin films were characterized using different techniques such as X-ray diffraction, UV-Vis spectroscopy, and scanning electron microscopy. To evaluate the photocatalytic properties of the Ag NP-doped ZnO thin films, the photocatalytic degradation of methylorange (MO) was monitored using a solar simulator. The antibacterial activity of the thin films was evaluated by measuring the inhibition of bacterial growth and further bacterial colonization of the tested substartes. Representatives of G- and G+ bacterial strains as well as eukaryotic pathogens were tested in direct contact with thin layers. The adhesion of bacterial cells and their subsequent ability to form a biofilm were evaluated.

Results and discussion: The XRD analysis results indicated that the crystalline structure of the ZnO thin films was not affected by Ag doping. SEM images show that the coatings are crack-free, and there is no agglomeration of the nanoparticles. The UV–Vis spectra of AgNP doped ZnO showed a typical absorption band in the visible range with a maximum at ~406 nm associated with the absorption of the local surface plasmon resonance (LSPR) typical of spherical metallic Ag nanoparticles. The degradation of MO increases from 75 to 95% from ZnO to AgNP doped ZnO coatings after 3h irradiation. The addition of Ag nanoparticles provides additional active sites for photocatalytic reactions to occur, leading to an increase in the overall degradation ratio of organic pollutants. Thin films showed differences in colonization by microbial representatives, and it is possible to consider their antibacterial potential.

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Poster / Bimetallic Fe-Zn oxides from spent pickling effluents for dye photocatalytic degradation

A. Ardila [1*], A. Ramírez Marín[2], L. Ocampo-Carmona[2], D. Ortiz-Muñoz[1], E. Arriola-Villaseñor[2], A. Talavera-López[3], A. Ortiz[4], G. Fuentes[5]

[1] *CAMER Research Group. Politécnico Colombiano Jaime Isaza Cadavid, Medellín, Colombia.*

[2]*Universidad Nacional de Colombia-sede Medellín, Colombia.*

[3]*Unidad Académica de Ciencias Químicas, Universidad Autónoma de Zacatecas, México.*

[4]*Tecnológico Nacional de México- Campus Instituto Tecnológico de Culiacán, México.*

[5] *Department of Process Engineering, Universidad A. Metropolitana Iztapalapa, México, D.F.*

**anardila@elpoli.edu.co*

Introduction. Hot-dip galvanizing processes generate wastewaters containing high concentrations of Zn (~ 150-200 g/L), Fe (~ 60-150 g/L) and HCl (~ 10-80 g/L) [1-2]. The increasingly stringent regulations regarding the discharge of heavy metals into the environment, and the increasing demand upon the recycling/reuse of these wastewater after proper treatment have focused our interest on the recovery of Fe and Zn from these industrial effluents for the development of new materials for photocatalic applications. Here we report the synthesis of Fe-Zn oxides active in the photocatalytic degradation of dyes (Reactive Blue 21 and Novacid Blue G 200) in simulated and real wastewater under visible and ultraviolet light.

Experimental/methodology: bimetallic Fe-Zn oxides were synthesized by coprecipitation and the photocatalytic tests were performed in cylindrical glass reactors containing 200 mL of 20000 mg/L blue dye solution under Vis light by 3 h.

Results and discussion. The different synthesized oxides are mainly composed of Fe and Zn in similar proportions (30- and 40% w/w) with a Fe:Zn ratio of 1:1. These relationships obtained are only possible for $ZnFe_2O_4$ heterolinked with Zn, which was corroborate by XRD. The oxidized materials with H_2O_2 showed better BET area results than those oxidized with $KMnO_4$, therefore, the calcined materials at 450°C presented double the surface area than those calcined at 600°C. In addition, the band Gap obtained in all the syntheses was around 1.2-1.4 eV, these values are below than those reported in the literature for similar materials (1.3-3.1 Ev) [2-3]. The XRD patterns were similar for all the samples, identifying characteristic peaks of zinc ferrite nanocrystals ($ZnFe_2O_4$) with a cubic spinel structure. However, peaks associated with the ZnO phase are also observed, suggesting an incomplete incorporation of the Zn^{2+} ions into the structure and evidencing that completely pure $ZnFe_2O_4$ was not obtained, which is consistent with the calcination temperatures used, since according to the literature this phase can be obtained completely pure at temperatures above 700 °C [3-4]. Dye degradation results (blue Novacido) of up to 100% were obtained for concentrations of water with real dyes from the ceramics industry. On the contrary, the degradation percentages for the reactive blue 21 with most of the materials were less than 40%, except with the K1.5-600, with which a degradation of 80% was obtained. Finally, the mineralization of dyes was thus evaluated through TOC measurements.

Table 1. Physicochemical characterization of the Fe-Zn based oxides and percentage of degradation.

Oxide Code	Fe (%)	Zn (%)	Surface Area (m^2/g)	pH_z	Band Gap (eV)	Novacid Blue G 200 Degradation (%)	Reactive Blue 21 Degradation (%)
K2-450	28.4	28.9	23.1	6.85	1.31	85.96	34.38
K2-600	29.8	29.0	12.0	7.03	1.31	70.88	47.46
K1.5-450	35.6	27.8	26.7	6.64	1.32	86.66	41.56
K1.5-600	36.5	28.9	12.7	6.93	1.28	91.42	82.26
K1-450	40.2	27.7	21.7	7.02	1.16	96.50	32.84
K1-600	36.6	28.1	12.4	6.89	1.14	100.00	34.92
H2-450	29.7	28.8	40.0	6.92	1.30	99.34	28.67
H2-600	31.5	29.2	19.7	6.84	1.38	100.00	35.82
H1.5-450	35.8	28.0	41.6	6.94	1.36	97.40	44.55
H1.5-600	40.6	29.5	17.1	6.23	1.28	100.00	41.58
H2-450	41.0	28.6	35.6	6.88	1.37	100.00	32.85
H2-600	36.3	28.2	21.0	6.83	1.38	100.00	32.01

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Doped ZnO Nanowires obtained by Chemical Bath Deposition for water remediation by photocatalysis: a screening approach

A. Baillard,[1*] E. Appert,[1] V. Jacob,[2] J. M. Becht[3] and V. Consonni[1]

[1] *Université Grenoble Alpes,CNRS,Grenoble INP,LMGP,F-38000 Grenoble, France*
[2] *Université Grenoble Alpes,CNRS,IRD, Grenoble INP,IGE,F-38000 Grenoble, France*
[3] *Institut de Science des Matériaux de Mulhouse IS2M, UMR CNRS 7361, UHA, 15 rue Jean Starcky, 68057 Mulhouse CEDEX, France*
**adrien.baillard@grenoble-inp.fr*

Keywords: ZnO, Photocatalyis, Dopant, Chemical bath deposition

Introduction. In one century, fresh water world demand has been multiplied by a factor of six [1] and hence new accessible and eco-efficient water treatment processes are needed. Advanced oxidation processes including heterogeneous photocatalysis are of high interest to address this challenge. Zinc oxide (ZnO) is a widely studied semiconducting material because it is non-toxic, bio-compatible, and offers a wide band gap energy (3.37 eV) that is favourable for electron-hole pair generation under UV light [2]. ZnO nanowires grown by chemical bath deposition (CBD), as an inexpensive, low-temperature and green chemistry compatible method, have emerged as highly promising. The extrinsic doping is an usual strategy to improve the photocatalytic activity through the generation of new energy levels in the bandgap aiming at limiting the electron-hole pair recombination [3]. However, the effect of extrinsic doping on the photocatalytic activity and processes of ZnO NWs is still highly debated and largely unknown.

Experimental/methodology. In this work, we investigate the extrinsic doping of ZnO nanowires with several elements such as Al, Ga, Cu, Sb and Cl using CBD [4-6] to assess their effects on the photocatalytic activity and processes. Several characterization techniques including scanning electron microscopy, X-ray diffraction, Raman spectroscopy, inductively coupled plasma-mass spectrometry (ICP-MS), and UV-visible absorption are performed to study the incorporation of dopants into ZnO nanowires and to deeply understand how it affects the photocatalytic reaction kinetics and processes during the organic dye degradation under UV light. The photocatalytic activity is followed by UV-visible spectroscopy to determine degration and kinetic rate. Ultra Performance Liquid Chromatography and ICP-MS are used to assay the dye degration pathway and ZnO NWs behavior.

Results and discussion. The effect of each dopant along with an additional thermal annealing to promote the degradation of Methtyl orange (MO) will be revealed and discussed in the light of its nature and optimal concentration. An influence of the nature of dopants on the MO degradation pathways and/or on the photocorrosion ability will also be reported and detailed.

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Inkjet printing of TiO_2 thin films doped with Cu_xO for photocatalytic water splitting

M. Navlani-García[1*], J. Chávez-Caiza[1], Liubov Belova[2], Cláudio M. Lousada[2], Á. Berenguer-Murcia[1], D. Cazorla-Amorós[1]

[1]*Materials Science Institute and Inorganic Chemistry Department, University of Alicante, Ap. 99, E-03080 Alicante, Spain*

[2]*Department of materials science and engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden*

[*]*Corresponding author. E-mail: miriam.navlani@ua.es*

Keywords: Photocatalysis, H_2, thin films, inkjet printing, heterojunction

Introduction.

Many key strategies to alleviate climate change focus on to the development of environmentally sustainable energy production and storage methods. Among these, utilizing H_2 as an energy vector (nowadays named "green hydrogen") clearly stands out [1-2]. In this respect, the catalytic decomposition of water into its elemental components triggered by light (i.e. photocatalytic water splitting) is an ideal candidate for future hydrogen production systems.

While powdered titanium dioxide (TiO_2) is one of the most widely studied catalysts, it has a band gap of 3.2 eV, and thus its absorption in the visible range is highly limited. Hence the composition and structure of TiO_2-based catalysts must be improved. Substantial efforts have been dedicated to the development of novel photocatalysts with enhanced visible light adsorption using different dopants [3], together with novel catalysts preparation techniques that may be incorporated in novel reactor architectures [4].

The objective of the present work is to prepare a series of photocatalysts based on the direct inkjet printing of nanoparticulate TiO_2 suspensions on suitable substrates, their subsequent modification by incorporating Cu species and the application of the resulting materials in the water splitting reaction under light irradiation.

Experimental/methodology.

The samples used in this study were prepared by direct inkjet printing of TiO_2 nanoparticles suspensions on microscope glass slides by applying the printing procedure for a different number of layers (ranging from 5 to 20) resulting in different thicknesses [5]. Some of the resulting TiO_2 films were subsequently doped with CuOx by impregnation with a $Cu(NO_3)_2$ solution followed by $NaBH_4$ treatment. The samples were placed into a quartz reactor containing a mixture of 7 mL of water and 1 mL of ethanol. The reactor was sealed with a rubber septum and the sample was irradiated for 6 h with a Hg lamp. The gas was analysed with a mass spectrometer after 6 h of reaction.

Results and discussion.

While the first results obtained in our study showed moderate H_2 production values after 6 h using only TiO_2 samples (0.2 µmol for the thin film prepared with 20 layers), incoporating Cu on the thin film enhanced H_2 production tenfold (1.9 µmol for the sample with 20 layers with incorporated Cu). The selection of a proper hole scavenger and the subsequent optimization of its concentration has allowed us to reach H_2 generation values which are very promising, which shows the applied value of our results.

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Efficient Removal of Antibiotics from Waste Water by Photocatalytically Active Supramolecular Organic–Inorganic Magnetic Composites

Sabina G. Ion, Octavian D. Pavel, Nicolae Guzo, Madalina Tudorache, Simona M. Coman, Vasile I. Parvulescu*, Bogdan Cojocaru*

Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Av., 030018 Bucharest, Romania
vasile.parvulescu@chimie.unibuc.ro, bogdan.cojocaru@chimie.unibuc.ro

Keywords: Hybrid composites, photocatalysis, antibiotics

Introduction. The complex chemical structure of the antibiotics and their biodegradation products made these very complicate pollutant residues. Their large diversity generated a large concern and, on these bases, considerable efforts have been made to identify an optimal treatment method for their removal. Among the various advanced oxidation processes, photocatalysis has emerged as a promising technology for wastewater treatment in general, and antibiotics removal in particular [1]. A key point in this scope is the identification of the photoactive structures capable to damage complex molecules with different chemical composition. With this aim we proposed a series of supramolecular organic-inorganic magnetic composites containing Fe or Zn-modified MgAl LDHs and M (Cu, Co, Fe, Ni)-phthalocyanine as photosensitizers. The activity of these photocatalysts was evaluated in the removal of *β*-lactam antibiotics from aqueous solutions under simulated light irradiation.

Experimental/methodology. The synthesis of Fe or Zn-LDH was carried out by the co-precipitation or mechanochemical method, using both inorganic and organic bases. The insertion of phthalocyanine started from a calcined LDH that has been mixed with a solution of M-phthalocyanine 3,4',4",4"'-tetrasulfonic acid. After the separation and washing, the solid was dispersed in a suspension of $FeCl_3$-$Fe_2(SO_4)_3$, and then precipitated with NH_4OH and then the produced solid was magnetically separated, washed and dried.

Results and discussion. The resulted composites were fully characterized using textural, spectral, and diffractometric techniques. The removal of ampicillin and amoxicillin antibiotics occurred via a two-step process i.e. a concerted adsorption and photocatalytic degradation. The loading of the adsorbed ampicillin was related only to the surface charge density of the sorbent surface. For the LDHs, the ampicillin-related amoxicillin was found to adsorb predominantly through a chemisorption mechanism, following a pseudo-second-order kinetics. Under a solar simulator as irradiation source, the composites with Zn-LDH prepared by co-precipitation showed the higher activity. A degradation of antibiotics as high as 98% (sample P7, figure 1) corresponded to a higher amount of phthalocyanine and the presence of large pores (124 Å) [2].

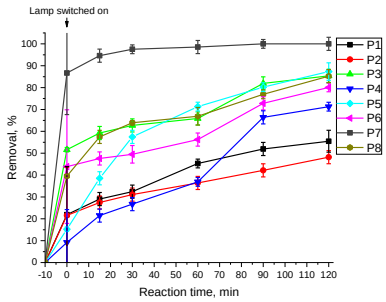

Figure 1. Removal of ampicillin from water solution using a solar simulator as irradiation source.

The degradation of β-lactam antibiotics followed two routes: hydroxylation and opening of the β-lactam ring. The ratio between these routes is influenced by the structure of the antibiotic and the nature of the catalyst.

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Photoelectrochemical H_2 production using g-C_3N_4/Sn_3O_4 photoanode

F. C. Romeiro[1]*, J. A. L. Perini[1], M. V. B. Zanoni[1], M. O. Orlandi[1]

[1]*São Paulo State University (UNESP), Institute of Chemistry, 55 Prof. Francisco Degni St, Araraquara, SP, 14800-060, Brazil*

[*]*costaromeirof@yahoo.com*

Keywords: tin oxide; graphitic carbon nitride; photoelectrochemical properties, hydrogen evolution reaction.

Introduction. The hydrogen gas (H_2) has attracted attention because its environmentally friendly burn with no emission of greenhouse gases [1]. The n-type Sn_3O_4 has been recently applied for H_2 generation. To avoid rapid rate of charge carrier recombination and improve photoelectrochemical performance in Sn_3O_4, the heterojunctions with g-C_3N_4 can be formed to overcome charge recombination at the interfaces of two compounds.

Experimental/methodology. Herein, Sn_3O_4 and g-C_3N_4/Sn_3O_4 heterostructure were synthesized via the microwave-assisted hydrothermal method, while g-C_3N_4 was obtained by the heating 1.5 g of melamine. The g-C_3N_4, Sn_3O_4 and g-C_3N_4/Sn_3O_4 working electrode were prepared by the spin coating methodology. The photoelectrochemical tests for H_2 generation took place at a sealed photoelectrochemical reactor equipped with a quartz window (electrolyte: 0.1 mol L^{-1} Na_2SO_4) and using solar simulator (300 W Xenon lamp). H_2 gas was identified and quantified using gas chromatography with a *thermal conductivity detector*.

Results and discussion. During photoelectrochemical experiments the g-C_3N_4/Sn_3O_4 presented highest photocurrent density of (1.2 mA.cm^{-2}). Transient photocurrent curves showed that the g-C_3N_4/Sn_3O_4 nanocomposite showed a quick response in the presence of light, indicating that the nanomaterial is sensitive to the UV-vis irradiation and presents faster charge separation [2]. The g-C_3N_4/Sn_3O_4 presented smaller resistance electron transport than that for the g-C_3N_4, Sn_3O_4, indicating that its charge transfer is faster as shown by Nyquist plots. The cumulative H_2 formation using all electrodes showed a stable production of H_2 for pure g-C_3N_4 and Sn_3O_4 materials within the investigated time period of 3 h, while for the g-C_3N_4/Sn_3O_4 a crescent generation of H_2 was observed until reach the maximum of 0.487 mmol L^{-1}. The H_2 production rate was nearly 4.4 and 4.8 times higher than the H_2 production using of g-C_3N_4 and Sn_3O_4 photoanode, respectively. This observation can be explained by the synergistic effect between Sn_3O_4 nanostructures and g-C_3N_4 nanosheets, in which the nanocomposite exhibited efficient separation of photoexcited electron–hole pairs, which decreased the recombination rate and therefore promoted higher H_2 generation.

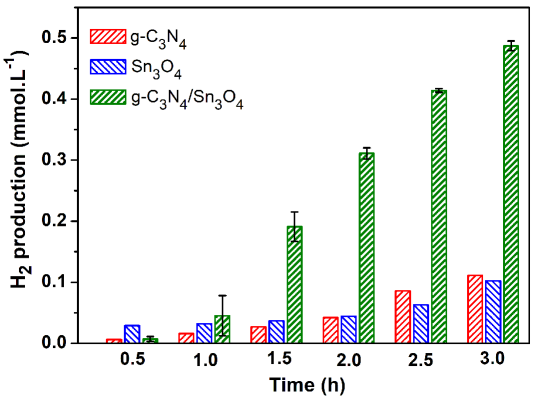

Fig. 1. Assessment of products formed after 3 h of photoelectrocatalytic H_2 evolution at g-C_3N_4, Sn_3O_4 and g-C_3N_4/Sn_3O_4 heterostructure electrodes under bias potential of 0.8 V vs. Ag/AgCl.

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Zeolite ZSM-5 Film-Supported Metal Oxides for Photocatalytic Decomposition of Volatile Organic Compounds

M.E. de Graaf[1,*], R.L. Riemersma[1], B. Baumgartner[1], R.J. Grijpma[1], A.-E. Nieuwelink[1], E.T.C. Vogt[1], E.M. Hutter[1], and B.M. Weckhuysen[1]

[1]*Utrecht University, Inorganic Chemistry and Catalysis, Institute for Circular and Sustainable Chemistry and Debye Institute for Nanomaterials Science, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands*

[*]*M.E.deGraaf1@uu.nl*

Keywords: photocatalysis, zeolite ZSM-5 films, volatile organic compounds,

Introduction. Harmful volatile organic substances (VOCs), which pollute many indoor environments [1], can be degraded by photocatalysts that absorb visible light. It is known that hybrid materials consisting of a zeolite support and a metal oxide are promising candidates for those degradation processes [1,2]. In addition, the zeolite support immobilizes the metal oxide nanoparticles (NPs) and provides a large surface area for the adsorption of VOCs. These materials can be incorporated in a coating that can be applied to walls or furniture as an air purifying coating. In this work, we use metal oxides supported on b-oriented zeolite ZSM-5 films to mimic a potential coating. We will show their optimization for VOC degradation and demonstrate a method to measure VOC photo-oxidation over film materials.

Experimental/methodology. Zeolite ZSM-5 films were synthesized (175 °C, 6 h) hydrothermally in a secondary growth medium (SGM) on glass supports (15x15 mm). The NPs were deposited by dropcasting. The fluoresent probe 2',7'-dichlorofluorescein (DCF) was used to assess the creation of radical oxygen species on TiO_2 NPs. A LED UV-lamp (λ_{max}=375 nm) was used to activate the NPs.

Results and discussion. A synthesis method for b-oriented zeolite films on glass has previously been developed in our group [3]. Herein, we have synthesised alumina-containing seeds (Si/Al=45) and grown these into continuous films using alumina containing SGMs (Si/Al = 45) (Figure 1A). This is promising since a higher alumina content can contribute to more efficient adsorption of VOCs. Next, these films were functionalized with cobalt oxide NPs (Figure 1B). Finally, we demonstrate a method by which we can evaluate the catalytic activity of our samples. Herein we use the fluorescent probe molecule DCF to assess the creation of radical oxygen species (ROS). Figure 1C shows that the fluorescence intensity increases over time, when a layer of TiO_2 NPs covered with a solution of DCF-precursor is illuminated with UV-light. This indicates that ROS are indeed being produced. We will apply this method to screen which zeolite films with deposited semiconductors are suitable for VOC photo-oxidation.

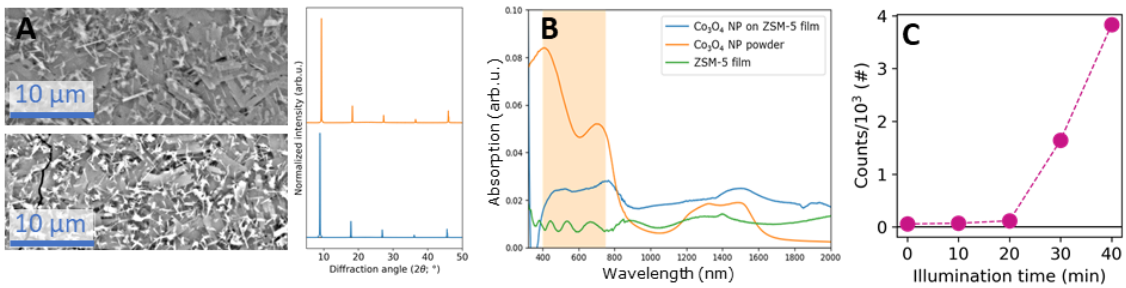

Figure 1: A) SEM images and XRD patterns of continuous b-oriented ZSM-5 zeolite films (SGM Si/Al=45) grown from Si/Al=45 seeds, B) UV-VIS spectroscopy data of cobalt oxide nanoparticles (NPs) (orange), the ZSM-5 zeolite film without NPs (green), the ZSM-5 zeolite film with NPs (blue), C) Fluorescence intensity over time of DCF probe molecule on TiO_2 nanoparticles on a glass substrate.

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TIO_2 AND TIO_2-CU_2O PHOTOCATALYTIC THIN FILMS DEPOSITED BY AA-MOCVD FOR MARINE ANTIBIOFOULING APPLICATIONS

Lisa Deblock[1*], Marianne Weidenhaupt[1] , Fabienne Faÿ[2] , Claire Hellio[3] and Carmen Jimenez[1]

[1]*Laboratoire des Matériaux et du Génie Physique, Univ. Grenoble Alpes, CNRS, Grenoble INP, 38000 Grenoble, France*
[2]*LBCM - Laboratoire de Biotechnologie et Chimie Marines, Université Bretagne Sud, 56100, Lorient, France*
[3]*LEMAR - Laboratoire des sciences de l'environnement marin, UBO, 29200 Brest, France*
**Orateur: DEBLOCK LISA, lisa.deblock@grenoble-inp.fr*

Keywords: marine biofouling, material interface, nanostructure, photocatalysis, thin films

Since 2003, the use of tributyltin (TBT) in antifouling coatings is prohibited because of its toxicity towards marine environments(1). The last decade has seen the emergence of a new research area : environmentally-friendly antifouling coatings. Combined with a non-toxic, corrosion-resistant character and good chemical stability in saline conditions, the photocatalytic properties of TiO_2 make this oxide a good eco-friendly antibiofouling alternative for marine environments(2). But even if it is showing promising results in in vitro experiments(3), the limited exposure to sunlight in the sea and the restricted absorbance range (UV) of TiO_2 in the solar spectrum are important issues. To enhance the antibiofouling properties, a combination of morphological and physico-chemical properties of TiO_2 is investigated.

In this context, TiO_2 thin films have been synthesized using Aerosol Assisted Metal Organic Chemical Vapour Deposition (AA-MOCVD). Using precise parameters, nanometric petals assembly (forming microflower-like structures) are obtained, enhancing the reactive specific surface of the material and thus its photocatalytic properties. By tuning some parameters of deposition, it is possible to vary the size and density of the flowers, and to investigate their influence on both the photocatalytic and antibiofouling properties of the material.
TiO_2-Cu_2O composite materials can be also synthesized by AA-MOCVD. This composite is expected to increase the photocatalytical activity through two phenomena. On one hand, according to Zhang et al.(4) , the substitution of Ti^{4+} by Cu^{2+}/Cu^{1+} in the TiO_2 lattice induces the creation of oxygen vacancies and additional impurity bands right above the valence band maximum of pure TiO_2, which results in a significant reduction of both band gap and the recombination rate of photoelectron–hole pairs, improving the photocatalytic performance and visible light absorption of TiO_2. On the other hand, the p-n heterojunction TiO_2-Cu_2O promotes the electron-hole separation and slow down the charges recombination(5).

The films morphologies, composition and photocatalytic performances are going to be investigated using SEM, DRX and a photocatalysis test, as well as their antifouling properties during in vitro experiments and marine immersion.

Acknowledgments
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The potential of spectral methods to be used in the characterization of photocatalysts

H. Drobná, L. Dubnová, V. Meinhardová, L. Smoláková, L. Čapek

University of Pardubice, Faculty of Chemical Technology, Pardubice, Czech Republic.
helena.drobna@upce.cz

Keywords: DRS UV-vis, Raman, DRIFT, spectroscopy, TiO_2, photocatalysts

Introduction. Heterogeneous photocatalysis belongs recently to the most studied environmentally friendly technologies for various applications. The most promising photocatalytically active semiconductor is TiO_2. In many respects (price, availability, low toxicity) the improving the properties of $TiO_2$is an interesting alternative for increasing quantum efficiency, decreasing the rate of electron-hole pair recombination, narrowing the bandgap. Electrochemical properties of photocatalytic material is closely related to its chemical, optical and textural structure. In this contribution, we provide an overview of the characteristics that can be obtained for photocatalysts by measuring DRS UV-vis, Raman and infrared spectra.

Experimental/methodology. Commercial (Sigma-Aldrich s.r.o., CR) and laboratory prepared (sol-gel method) TiO_2 photocatalysts were used as reference materials. The photocatalytic activity of the photocatalyst samples was tested by means of the amount of H_2 evolved during the photocatalytic decomposition of the aqueous methanol solution in batch reactor equipped by UV-LED solo P lamp with parallel beam optics ($\lambda = 365$ nm, 5 W). Diffuse reflectance (DR) UV-vis spectra of photocatalysts were measured in quartz cuvettes by using a GBS CINTRA 303 spectrometer (GBC Scientific Equipment, Australia). Samples were also studied by Raman spectroscopy using a Raman DXR Thermo Scientific DXR SmartRaman (Nicolet CZ s.r.o., CR) equipped by the Nd:YAG laser. Temperature resolved IR spektra were measured in DRIFT cell Praying Mantis™ by FTIR spectrometer Nicolet iS20 (both Nicolet CZ s.r.o., CR).

Results and discussion. The refelctance (DR UV-vis) was recalculated into the dependence of Kubelka–Munk function ($F(R\infty)$) on the absorption energy using the equation $F(R\infty) = (1 - R\infty)^2 / (2 \cdot R\infty)$, where $R\infty$ is the diffuse reflectance from a semi-infinite layer. The obtained spectra were transformed to the dependencies $(\alpha h\nu)^2$ or $(\alpha h\nu)^{1/2}$ against hv. Absorption coefficient (α) is approximately equal to $F(R\infty)$. Depending on the sort of semiconductor the direct and indirect band gap energy values (Eg) were determined by extrapolating of straight line of $(\alpha h\nu)^2$ or $(\alpha h\nu)^{1/2}$ to zero. Raman spectra of studied photocatalysts determine the phase composition of TiO_2. In addition the exact position and the width of individual peak is affected by sizes of nanoparticles and a presence of defects of anatase structure. Structural changes of the precursors depending on the calcination temperature were studied using DRFT spectroscopy. The correlation between measured chemical, optical and textural properties and photocatalytic activity of tested photocatalysts were suggested.

Application of Indirect Techniques of EPR Spectroscopy in Heterogenous Photocatalysis

Zuzana Dyrčíková, Kristína Czikhardtová, Dana Dvoranová*

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic
**dana.dvoranova@stuba.sk*

Principle of the heterogeneous photocatalysis, as one the effective advance oxidation proccess (AOP) method, can be define as follows – *change in the rate of a chemical reaction or its initiation under ultraviolet (UV) or visible (VIS) irradiation in the presence of a substrate, the photocatalyst, that harvests light and is involved in the chemical transformation of the reaction partners*. One the most studied photocatalysts are metal oxides, such titanium dioxide or zinc oxide, however their Achilles' heel is absorption only in UV region. Nowadays the main target si preparation of photocatalyst active upon solar light. The modification with other semiconductors or metals/non-metals doing/decorating have been proposed to improve the charge carrier separation and better absorption in the VIS region. Novel photocatalytic materials are closely coupled with their potential photoactivity and capability of the generation of various reactive paramagnetic species and the electron paramagnetic resonance (EPR) spectroscopy represents a sensitive spectroscopic method that allows the detection and characterization of these paramagnetic centres in different semiconducting nanomaterials which are significant for their photocatalytic properties. Although EPR provides direct detection of free radicals, in photocatalytic investigations utilizitation of indirect techniques, such spin trapping, spin scavenging, oxidation of sterically hindered amines or photoreduction, is often applied (Fig. 1). The evaluation of the photocatalytic activity of individual titania structures is based on the nature and quantity of reactive radical intermediates generated in the irradiated semicondutor suspensions obtained by in situ EPR spectroscopy. Proper choice of suitable experimental conditions is crucial for their successful application in heterogeneous semiconductor systems and can help to gain a comprehensive picture of the photoinduced processes undergoing upon light exposure of the photocatalyst in suspensions [1-3].

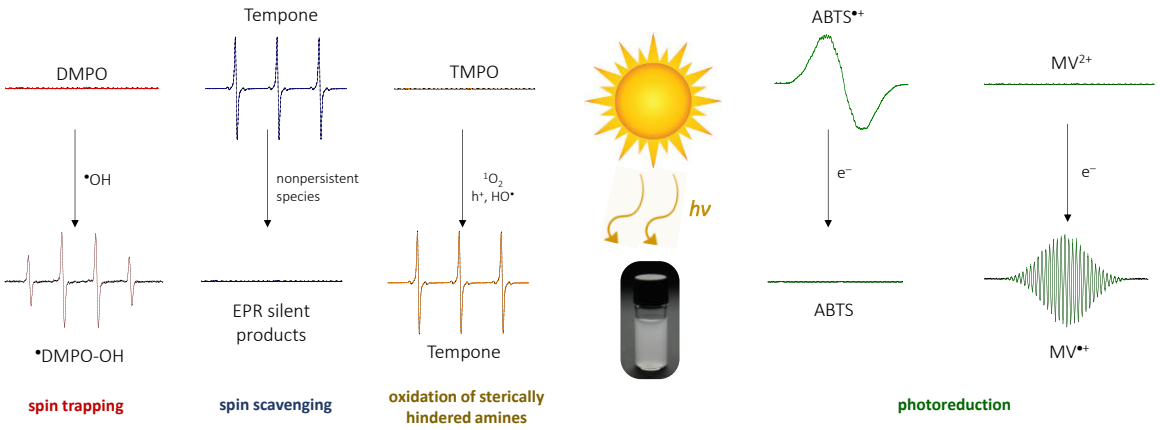

Fig. 1 Scheme of selected indirect EPR techniques applied in the detection and characterization of transient paramagnetic species.

Acknowledgments
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Investigating the Transient Behaviors during Photocatalytic NO Oxidation

S.Ernam[1], D.Üner[1*]
[1]*Middle East Technical University, Ankara, Turkey*
[*]*uner@metu.edu.tr*

Keywords: Photocatalysis, NO oxidation, light intensity, water injections

Introduction. Photocatalytic NO oxidation reaction is a standard diagnostic tool for photocatalytic activity. The reaction can be used to investigate the bottlenecks of photocatalysis. One of the distinct features of photocatalytic NO oxidation is the transient period of NO conversion observed, following the beginning of illumination. NO conversion reaches a steady state only after a certain period of time, and the nature of this behavior depends strongly on parameters such as the illumination intensity and the concentration of the reactants, in particular the moisture content.

Experimental/methodology. Experiments were performed according to the protocols described by the ISO Standard (22197-1-2007). The experiment set up consists of three mass flow controllers to adjust a desired ratio of moist air, dry air and NO, a photoreactor which houses a catalyt coated flat plate and a NO_x gas analyzer. In this study, TiO_2 P25 was used as catalyst. Illumination intensity and moisture content were varied independently to investigate their effects on the reaction behavior. Light intensity and humidty levels were measured with home made embedded devices using the FRDM K64F microcontroller board.

Results and discussion. Experiments revealed that at higher light intensities, the reaction starts with a very high conversion and needs longer times to reach its steady state at a lower conversion value. In contrast, experiments with low light intensities reach their steady conversion levels, proportional to the intensity, almost immediately after the reaction starts, as shown in Figure 1. The relationship between the steady state reactant conversion and light intensity is given as insert in Figure 1. Furthermore, the effect of water injections to the system was also investigated using a specially built relative humidity measurement device. The water injection transient data revealed the qualitative nature of the interactions. Effect of water injections on NO conversion and relative humidity at two different ilumination intensities can be seen in Figure 2. Finally, impact of time spent under reaction conditions without NO presence was studied. It was shown that humid air stream and illumination is significant for the transient period, as shown in Figure 3. The results of this study show that careful consideration has to be given to the experimental parameters for the accurate assessment of photocatalytic activity through NO oxidation reaction.

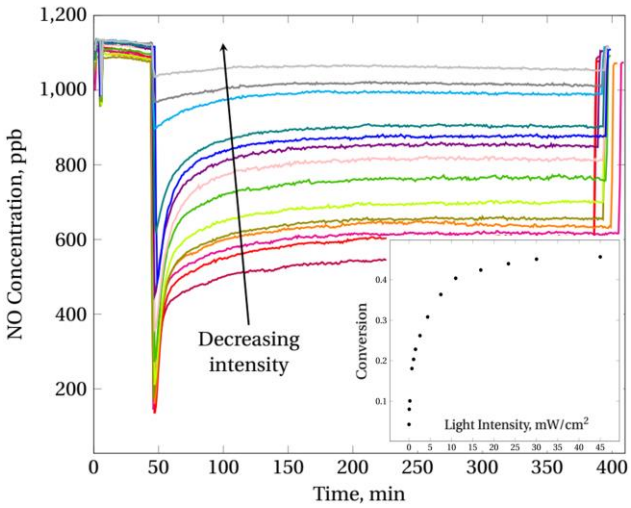


Figure 1 Effect of light intensity on NO oxidation.

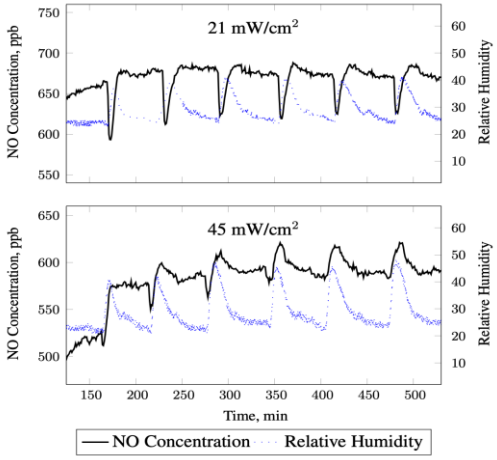


Figure 11 Effect of water injection on relative humidity and NO conversion

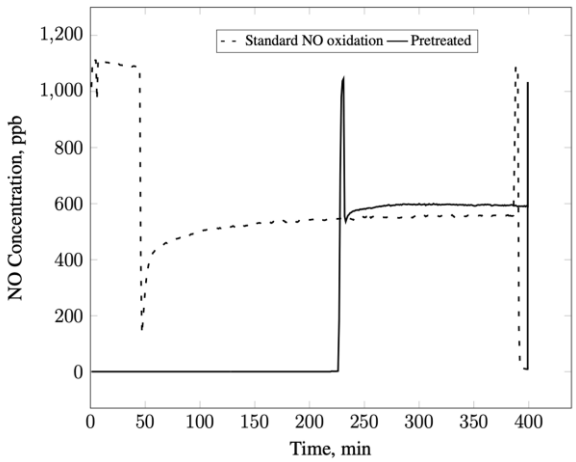


Figure 3 Effect of moist air and illumination pretreatment on the transient behavior.

$CuFe_2O_4$ as efficient photoactive materials for degradation of organic pollutant

Sridhar Gowrisankaran[1*], Hryhorii Makarov[2], Martin Motola[1], Olivier Monfort[1*]

[1]*Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University Bratislava, Slovakia.*

[2]*Department of Experimental Physics, Faculty of Mathematics Physics and Informatics, Comenius University Bratislava, Slovakia*.

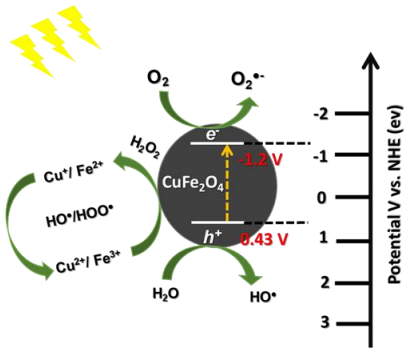
gowrisankaran1@uniba.sk

Keywords: photocatalysis; Fenton; synergy; $CuFe_2O_4$

Introduction. Due to the formation of highly reactive oxygen species, which have the ability to oxidize and mineralize organic molecules, advanced oxidation processes (AOPs) are effective at degrading organic pollutants in water [1,2]. Particularly in heterogeneous systems, photocatalysis and Fenton-based processes are among the most investigated AOPs. Copper ferrite ($CuFe_2O_4$) is known as promising photocatalyst due to its attractive energy band gap (E_g) in the visible light (E_g = 1.7–1.9 eV), low cost, good photochemical stability and high specific surface area [3]. In addition, the advantage of such a material is the possibility to also trigger Fenton-based processes since $CuFe_2O_4$ contains Fenton active elements (Fe and Cu) [4]. The goal of this work is to assess a potential synergy between photocatalysis and Fenton-based processes which is scarcely described in the literature.

Experimental. In a typical synthesis, cupric and ferric nitrate precursors are combined with a surfactant (PEG) in a solution, which is then processed by hydrothermal method (160°C for 24 hours). The resulting powders are dried at 80 °C overnight and the crystalline phase composition and surface morphology of the materials is investigated by XRD and SEM, respectively. Different photochemical systems are investigated (type of light, type of radical precursor, etc.) and during the degradation of caffeine, and the contribution of the different involved photo-induced processes is determined.

Results and discussion.



Based on SEM and XRD analyses, the morphology and crystalline phase composition of $CuFe_2O_4$ is discussed: nanoparticles of spinel structure are confirmed. Concerning the degradation of caffeine, the effect of surfactant concentration is studied. Further, with PEG optimized concentration the efficient of different photochemical systems is compared, while the iron leaching is also studied to assess whether homogenous Fenton reaction has a significant role or not.

Acknowledgments

This work is partially supported by the Slovak Research and Development Agency under the contract No. APVV-21-0039, the Scientific Grant Agency of the Slovak republic (VEGA project No. 1/0319/23), and USCCCORD project co-financed by the European Regional Development Fund within the Operational Programme Integrated Infrastructure (ZoNFP: NFP313020BUZ3).

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Gas Phase Deposition of Well-defined Bimetallic Gold-silver Clusters for Photocatalytic Applications

Vana Chinnappa Chinnabathini[1,2,3], Fons Dingenen[2,3], Rituraj Borah[2,3], Imran Abbas[1], Johan van der Tol[1], Zviadi Zarkua[1], Francesco D'Acapito[4], Thi Hong Trang Nguyen[1], Peter Lievens[1], Didier Grandjean[1*], Sammy W. Verbruggen[2,3], Ewald Janssens[1]

[1]*Quantum Solid-State Physics, KU Leuven, 3001 Leuven, Belgium.*
[2]*Sustainable Energy, Air & Water Technology (DuEL), University of Antwerp, 2020 Antwerpen, Belgium.*
[3]*NANOlab Center of Excellence, University of Antwerp, 2020 Antwerpen, Belgium.*
[4]*CNR-IOM-OGG c/o ESRF LISA CRG - The European Synchrotron, 38043 Grenoble Cedex 9, France*
* didier.grandjean@kuleuven.be

Keywords: Plasmonic photocatalysts, AuAg bimetallic gas-phase clusters , XAFS, TiO_2, Self-cleaning.

Introduction. Cluster beam deposition is employed for fabricating well-defined bimetallic AuAg plasmonic photocatalysts for visible light self-cleaning surface applications[1,2] to enhance their activity while facilitating a more fundamental understanding of their structual and catalytic properties.

Experimental/methodology. Au_xAg_{1-x} clusters with compositions (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1) spanning the metals miscibility range were produced in the gas-phase by laser ablation of bulk alloyed targets of the corresponding compositions[3] and soft-landed on TiO_2 P25-coated silicon wafers with an optimal coverage of 4 atomic monolayer equivalents.

Results and discussion. Electron microscopy images show that at this coverage most clusters remain well dispersed whereas EXAFS data are in agreement with the finding that the deposited clusters have an average size of *ca*. 5 nm and feature the same composition as the ablated alloy target.[3] A composition-dependant electron transfer from Au to Ag that is likely to impart chemical stability to the bimetallic clusters and protect Ag atoms against oxidation is additionally evidenced by XPS and XANES.[4]

Under simulated solar light, Au_xAg_{1-x} clusters show a remarkable composition-dependent volcano-type enhancement of their photocatalytic activity towards degradation of stearic acid, a model compound for organic fouling on surfaces. The Formal Quantum Efficiency (FQE) is peaking at the $Au_{0.3}Ag_{0.7}$ composition with a value that is twice as high as that of the pristine TiO_2 P25 under solar simulator.[4] Under UV the FQE of all compositions remains similar to that of pristine TiO_2. A classical electromagnetic simulation study confirms that among all compositions $Au_{0.3}Ag_{0.7}$ features the largest near-field enhancement in the wavelength range of maximal solar light intensity, as well as sufficient individual photon energy resulting in a better photocatalytic self-cleaning activity. This allows ascribing the mechanism for photocatalysis in the visible mostly to the plasmonic effect of the bimetallic clusters through direct electron injection and near-field enhancement from the resonant cluster towards the conduction band of TiO_2. These results not only demonstrate the added value of using well-defined bimetallic nanocatalysts to enhance their photocatalytic activity but also highlights the potential of the cluster beam deposition to design tailored noble metal modified photocatalytic surfaces with controlled compositions and sizes without involving potentially hazardous chemical agents.

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Propionic acid decomposition by the multi-decorated TiO_2-based photocatalysts under visible light irradiation

N. Haghshenas[1*], G. Falcone[1], E. Falletta[1,2], C.L. Bianchi[1,2]

[1]Dipartimento *di Chimica, Università degli studi di Milano, Via Golgi 19, 20133, Milano, Italy*

[2] *Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via Giusti 9, 50121, Firenze, Italy.*

[*]*Niloofar.haghsenas@unimi.it*

Introduction. Unpleasant odors are the most disturbing pollutants and the main reason for air quality complaints in urban and industrial areas. Odor emissions consist of various chemical components, some of which can be perceived at very low threshold levels.[1] Volatile organic compounds (VOCs) have been designated as the major odorant group. In particular, volatile fatty acids (VFAs) represent an important source of unpleasant odors that have been considered in many studies. Among them, propionic acid (PA) has attracted much attention as one of the leading compounds responsible for the odors-polluted environment.[2]

In this work, the effect of multi-decorated enhanced photocatalysts, for the PA decomposition, under visible light irradiation, was properly investigated.

Experimental/methodology. Micrometric TiO_2 by Kronos (identified as 1077) was multi-decorated by three noble metals (Ag, Pt, and Au) through a multistep approach. At first, Ag NPs from Ag-enriched wastewater solution were properly prepared by a previously developed method [3] and 8%Ag-TiO_2 photocatalyst was obtained by impregnation method and calcined in the air at 400°C. The final material underwent further decoration by the other metals (Pt and Au). A secondary decoration of Ag-TiO_2 was carried out by Au, Pt, and bimetallic AuPt NPs, prepared by chemical reduction. Also, in this case NPs were prepared from metals-enriched wastewater solution. The secondary decoration of Ag-TiO_2 was done by impregnation as well. All the prepared photocatalysts were characterized by targeted physico-chemical techniques. The PA decomposition tests were performed in a 5.5L Pyrex reactor containing 0.5 ppm of PA in the vapor phase, in the presence of 50 mg of each photocatalyst, under LED light irradiation (P= 2450 LUX) for 190 minutes. The progress of the reaction was monitored by an online GC/FID instrument.

Results and discussion. Figure 1 reports the results obtained in the photodegradation of PA by the prepared photocatalysts.

As expected, bare TiO_2 Shows no photoactivity towards PA degradation under visible light irradiation. The first decoration with 8%(wt) Ag NPs leads to a significant increase in photoactivity, reaching a percentage of PA photodecomposition higher than 40% in three hours. The effect of the secondary decoration is strongly related to the type of metal used. If, on the one hand Au@Ag-TiO_2 exhibits poorer activity with respect to Ag-TiO_2, on the other hand Pt@Ag-TiO_2 can decompose about 60% of PA in two hours.

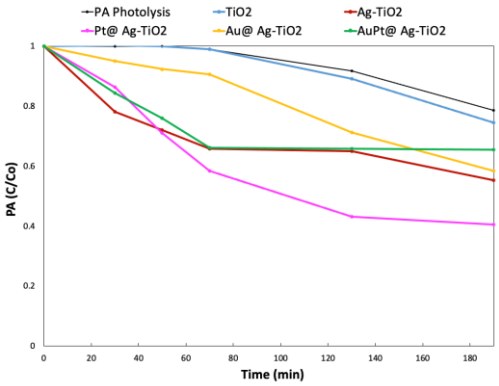

Figure 1. Photoactivity graph of PA

AuPt@Ag-TiO_2 photocatalyst balances the negative aspect of Au NPs with the positive ones of Pt NP, effectively showing the same activity of Ag-TiO_2.The enhanced photoactivity of Pt@Ag-TiO_2 could be ascribed to both the localized surface plasmon resonance (LSPR) effect from Ag NPs and the "Electron sink" effect from Pt NPs. In contrast, the poor performances of Au@Ag-TiO_2 are mainly due to the different transformation products (identified by GC-MS), which negatively affect the Au NPs.

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Green hydrogen generation from photocatalytic water splitting using PGM modified TiO_2

Naomi Harrisankar*, Eric van Steen

**Catalysis Institute, Department of Chemical Engineering, University of Cape Town, South Africa.*

*hrrnao001@myuct.ac.za

Keywords: Photocatalysis, water-splitting, green hydrogen

Introduction. The generation of green hydrogen from photocatalytic water splitting using sunlight and a semiconductor photocatalyst could provide a route for sustainable energy storage in the form of hydrogen. However, photocatalysts suffer from low efficiencies. TiO_2-P25 has become a benchmark catalyst in photocatalysis, despite its low efficiency as a consequence of its large bandgap, thus reducing the portion of the electromagnetic spectrum that a photocatalyst can absorb, as well as the high recombination rates and thus reducing the charge carriers that take part in the surface reactions.[1] Here, we show that TiO_2 can be modified using PGM nanoparticles to improve its efficiency via two phenomena: Schottky barrier formation and surface plasmonic resonance. A Schottky barrier created at the semiconductor-metal interface may act as an electron trap, prolonging the lifespan of the charge carriers. The photocatalyst's light absorption ability was investigated by varying nanoparticle morphology. [2]

Experimental/Methodology. Spherical, cubic and nanorod PGM nanoparticles (Pt, Pd and Ru) were loaded onto TiO_2 (P25 Degussa). The catalysts have been characterised using XRD, TEM, UV-VIS, TPR, and TPO. The photocatalytic activity was studied in a batch slurry photoreactor using UV-A, UV-C, and visible light. Furthermore, we present the role of a sacrificial agent and probe further into the catalyst-light relationship by varying light energy and intensity.

Results. The hydrogen production depends linearly on the number of photons (see Figure 1 (a)). The rate of H_2 formation increases upon the addition of PGMs, which is related to the metal work function and Schottky barrier.

The photo-catalytic water-splitting is often studied in the presence of a sacrificial agent (e.g. ethanol), which improves the rate of H_2 formation significantly (Figure 1(b) and (c))as ethanol acts as an electron donor reducing electron-hole recombination. Furthermore, we show the effect of nanoparticle morphology on the absorption ability of the photocatalyst using UV-VIS and reactor studies.

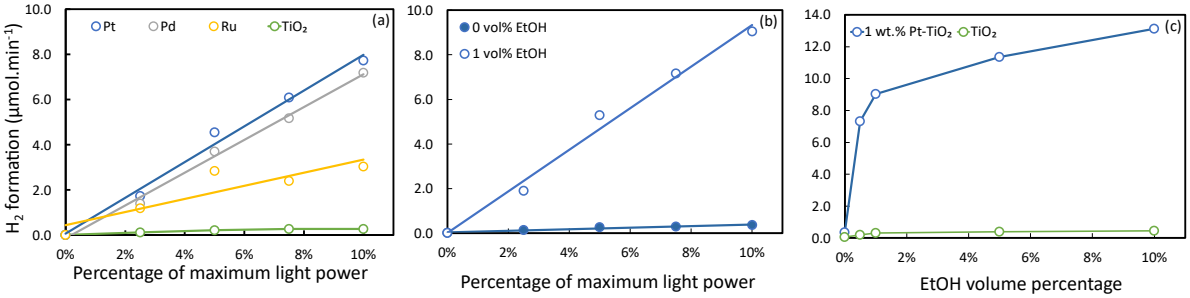

Figure 1: Rate of H_2 formation ras a function of percentage of maximum power for (a) various PGM loaded TiO_2 photocatalysts, (b) effect of sacrificial agent and (c) Rate of H_2 formation as a function vol. % of sacrificial agent

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Enhanced Photocatalytic Hydrogen Evolution of ZIF-8/$CuWO_4$ Hybrid Structures

M. U. Iqbal[1*], M. Zitnan[1], O. Sisman[1], L. Wondraczek[2], D. Galusek[1, 3], J. Velazquez[1]

[1]*Centre for functional and surface functionalized glass, Alexander Dubček University of Trenčín, Trenčín, Slovakia*

[2]*Otto-Scott Institute for Material Research, Friedrich Schiller University, Jena, Germany*

[3] *Joint Glass Centre of the IIC SAS, TnUAD, and FChPT STU, Trenčín, Slovakia*

*muhammad.iqbal@tnuni.sk

Keywords: Heterojunction, Metal organic Frameworks (MOFs)

Introduction. $CuWO_4$, as a semiconductor-based photocatalyst with a moderate bandgap (2.2–2.4 eV), has been attracting considerable attention as a promising candidate for H_2 generation. Despite that, $CuWO_4$ does not show significant improvements in photocatalysis for hydrogen evolution reaction. A possible explanation is that the midgap states created by the empty Cu(3dx2-y2) could restrict the mobility of the carriers. Thus, $CuWO_4$ has to be modified, as a heterojunction to improve its electron transfer kinetics and properties [1]. Additionally, the heterojunctions between metal oxide-based semiconductors and metal-organic frameworks (MOFs) like Co-based ZIF-67 [2], TiO_2/MIL-101 [3], and ZnO/MIL-53 [4] have been used as photocatalysts due to their high ability of charge separation, greater surface area and light absorption. In the present work, we modified $CuWO_4$ nanoparticles with ZIF-8 to increase the surface area, broaden their light absorption region and inhibit the recombination of photogenerated electrons to these semiconductors, thus promoting their photocatalytic performance.

Experimental/methodology. $CuWO_4$ was prepared by co-precipitation method, while $CuWO_4$ hybrid composites were prepared by an in situ-growth method. XRD, SEM, FTIR, and XPS were used to inspect the structure.

Results and discussion. The ZIF-8/$CuWO_4$ hybrid structures were synthesized, as confirmed by XRD, FTIR (Figure 1 and 2), and XPS. The as-synthesized composites contain both $CuWO_4$ and ZIF-8 phases. Due to this, the band gap of ZIF-8 was reduced from 5.22 to 3.5 eV, as confirmed by DRS-UV-Vis spectroscopy (Figure 3 and 4). The minimum energy required to split water into H_2 and O_2 is 1.23 eV and four photons are needed for this reaction to occur. The ideal band gap of photocatalyst lies in between 2 to 3.5 eV for the effective absorption of light spectra, as the ZIF-8/$CuWO_4$ hybrid structures show similar band gap of 3.5 eV, therefore, the photocatalytic enhancement is expected.

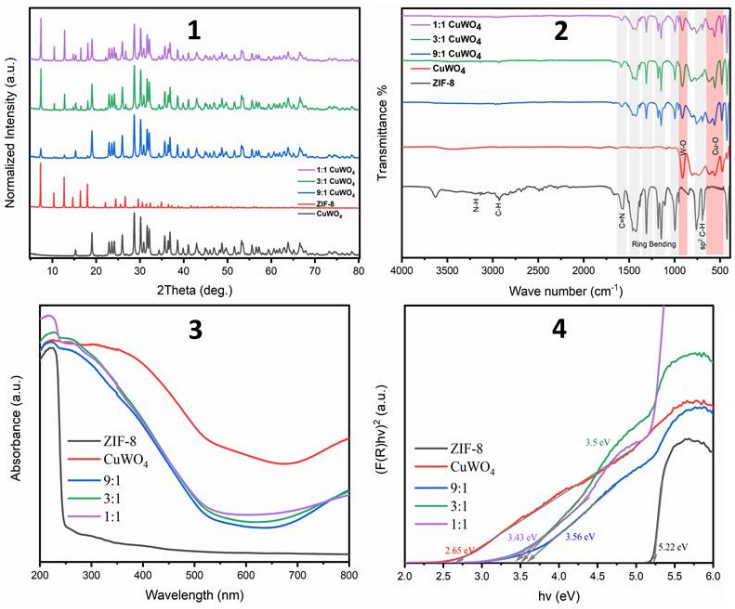

Figure 1 XRD, 2 FTIR graphs, 3 Absorbance UV-Visible DRS, and 4 Kubelka-Munk Plot for pure ZIF-8, $CuWO_4$ and their hybrid structures

Acknowledgments

This project has received funding from the FunGlass PHD grant no. 22_05 and VEGA 1-0844-21. This paper is a part of the dissemination activities of project "FunGlass" (Centre for Functional and Surface Functionalized Glass). This project has received funding from the European Union´s Horizon 2020 research and innovation program under grant agreement no. 739566.

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Photocatalytic Water Decontamination: Fe-C/g-C_3N_4 Catalyst in Action on Vltava River.

N. Ishak[1*], M. Šoóš[1], M. Grandcolas[2]

[1] *University of Chemistry and Technology, Technická 5, Prague, Czech Republic*

[2] *SINTEF Industry, Department of Sustainable Energy Technology, Forskningsveien 1, 0373 Oslo, Norway*

Corresponding author: ishakj@vscht.cz*

In this study, a photocatalyst composed of Fe-C/g-C_3N_4 was synthesized using a wet impregnation method and was evaluated for its effectiveness in decontaminating water from the Vltava River. The composite photocatalyst was activated through temperature treatment and was characterized using various techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), thermal gravimetric analysis (TGA) and ultraviolet-visible spectroscopy (UV-Vis). The results showed that the catalyst was able to effectively remove bacteria from the water in few minutes under sunlight. The sample with the highest catalytic activity in degrading bacteria was identified. The optimal amount of catalyst in the medium was determined through experiments conducted under a solar simulator lamp for one hour. The reason behind the high activity of the Fe-C/g-C_3N_4 photocatalyst was also explored and it was found that the enhancement in the electrochemical properties was a result of the doping of iron and carbon, as well as heat treatment. The performance of the catalyst was also tested when it is embedded in an electrospun membrane and the results were compared to the case of the slurry application. Overall, this study suggests that Fe-C/g-C_3N_4 photocatalyst is a cost-effective, efficient and innovative method for green water decontamination, due to its high activity, low cost and non-toxicity.

MoS_2 nanomaterials as efficient photocatalysts in Advanced Reduction Processes (ARPs)

Joanna Kisała

[1] *Institute Biology and Biotechnology, College of Natural Sciences, University of Rzeszow, Rzeszow, Poland*
[*] *jkisala@ur.edu.pl*

Keywords: photocatalysis, advanced reduction processes, reaction kinetic

Introduction. The major environmental challenge are organic compounds resistant to degradation under natural conditions. This group of compounds includes dyes, pesticides, pharmaceuticals, personal care products. One of the prominent goals of environmental studies has, therefore, been to degrade these substances to preferably harmless and easily disposable compounds. Although Advanced Oxidation Processes (AOP) are one of the widely used techniques for removing organic pollutants [1], they are not suitable in all cases (e.g. oxidative photodegradation of polyhalogenated compounds is kinetically unfavored [2]). Hence, reductive methods can be considered as an alternative degradation method [3]. In the present study, MoS_2 was examined as photocatalysts for two dyes degradation: methylene blue (MB) and bromophenol blue (BPB). The degradation processes were conducted under reductive conditions.

Experimental/methodology. A solution of dye (methylene blue MB, or bromophenol blue BPB) with suspended catalyst (MoS_2) was illuminated (power density 4.7 $mW \cdot cm^{-2}$) for 120 min. Analysis of the reaction progress was carried out by UV-Vis measurements of dyes decay and potentiometric measurements of an increase in bromide concentration. The reaction was conducted under reduction conditions with continuous argon flow (for oxygen removing) and in the presence of t-BuOH as a hydroxyl radical scavenger.

Results and discussion. The morphology and structure of catalyst were characterised by SEM, XRD, AFM, XPS spectroscopy, Raman spectroscopy, UV-Vis spectroscopy, and zeta potential measurements. The observed diffraction peaks in XRD spectrum revealed 2H phase of MoS_2 with average size of crystallite 50 nm. The estimated band gap 2.03 eV indicates good optical response to UV-Vis irradiation. The progress of photocatalytic degradation was monitored by recording changes in the dyes concentration. The substrate decay obeys the pseudo-first-order kinetics according to equation: $\ln C_t/C_0 = -k_{app}t$. The half-lives of decay ($t_{1/2}$) were 9.1 min and 17.3 min for BPB and MB, respectively. The apparent rate constant k_{app} calculated from plots was 155.6×10^{-3} min^{-1} and 81.7×10^{-3} min^{-1} for BPB and MB, respectively. Observed for BPB debromination directly indicates the reducing pathway of BPB degradation. For establishing of degradation pathway, the kinetic simulations were performed with the KINETISCOPE™ stochastic kinetic simulation software. Based on the obtained kinetic results and simulations of the kinetics of the dyes degradation reaction, a suitable reaction pathway has been proposed.

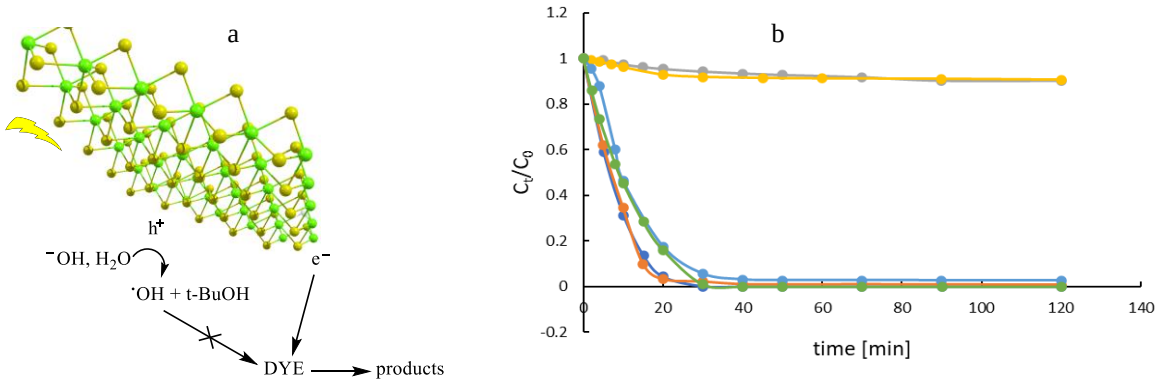

Figure 1. Schematic description of dye photocatalytic degradation (a); dyes decay in time in: photolytic process for MB (yellow), photolytic process for BPB (gray), degradation of MB (light blue), simulation of MB decay (light green), degradation of BPB (orange), simulation of BPB decay (blue) (b)

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Advanced oxidation process for degradation of textile microplastic in wastewater

M. Kocijan [1*], T. Radošević [2], L. Einfalt [2], N. Gračanin [2], D. Vengust[3], M. Podlogar[2]

[1] *Department of Materials, Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Zagreb, Croatia*
[2] *Department for Nanostructured Materials, Jožef Stefan Institute, Ljubljana, Slovenia*
[3] *Advanced Materials Department, Jožef Stefan Institute, Ljubljana, Slovenia*
[*] *martina.kocijan@fsb.hr*

Keywords: textile microplastic, TiO_2 catalyst, photocatalysis, degradation

Introduction: The synthetic plastic industry is one of the fastest-growing industries in the world producing a wide range of products necessary for life. Textile industry is also among them and it is considered as one of the major sources of microplastic pollution. Textile microplastics are usually in the form of fibers, and their main source of release is their production and household washing. Consequently, microplastics (1 µm to 5 mm) end up in aquatic and terrestrial ecosystems and become one of the most serious environmental concerns. Its long persistence in the ecosystem threatens the health of humans, animals, etc. [1], [2].

The development of reliable technologies for removal of microplastic pollutants is receiving more attention nowadays, including physical, chemical, and biological treatment. Conventional processes are not effective, because thei removal is only physical separation from the water, and requires post-treatment for the complete degradation of microplastic pollutants. Advanced oxidation processes (AOPs) can completely remove of pollutants to non-hazardous molecules such as CO_2, H_2O, and mineral acids [3].

Heterogeneous photocatalysis is a method that uses light and catalyst to produce reactive oxygen species (ROS), known as radicals. Produced radicals have a high redox potential, e.g. hydroxyl radicals E° = 2.72 V, which can easily attack the molecular structure of various pollutants and completely convert hazardous organic pollutants into harmless products [4]. Furthermore, TiO_2-based photocatalysis can break bonds in plastics with the assistance of light.

Experimental/methodology. Photocatalytic degradation was performed on commercially available pure textile microplastic fibers such as polyethylene terephthalate (PET), polyamide (PA), and polypropylene (PP). Microplastic fibres were dispersed in an ultrapure aqueous suspension of TiO_2 catalyst. The photocatalytic tests were carried out using simulated solar light (300W Osram Ultra Vitalux bulb) as a source of irradiation. Microplastic fibres were characterised before and after photocatalytic treatment using a scanning electron microscope (SEM) and Raman spectroscopy in a range from 400 to 3300 cm^{-1}.

Results and discussion. The morphology of fiber's surface before and after photocatalytic treatments were analyzed. SEM analysis reveals that the surface of fibers is smooth before, while after the treatment under the simulated solar light in presence of TiO_2, is damaged. The deformations on the fibres are numerous and very obvious for PA fibres, and the less pronounced for PP microfibers. Further Raman analysis confirmed structural changes of plastics, which enable correlation between SEM and Raman methods. For future work, we expect to increase the rate of the degradation process with functionalization of TiO_2 nanocrystals.

Acknowledgments

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Effect of the photocatalytic activity of TiO_2 on preparation method for CO_2 reduction and water splitting

M. Filip Edelmannová[1*], K. Kočí[1], M. Reli[1], P. Nadrah[2], A. Škapin Sever[2], U. Štangar Lavrenčič[3]

[1]*Institute of Environmental Technology, CEET, VŠB-TUO, 17. Listopadu 15/2172, Ostrava-Poruba, 708 00, Czech Republic*

[2]*Slovenian National Building and Civil Engineering Institute, Dimičeva ulica 12, 1000 Ljubljana, Slovenia*

[3]*University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana, Slovenia*

[*]*miroslava.filip.edelmannova@vsb.cz*

Keywords: CO_2 reduction, TiO_2, photocatalysis, effect of pH, sol-gel, hydrothermal method

Introduction. The global warming and carbon dioxide emissions represent serious concerns for the developed countries. Efficient conversion of CO_2 into fuels would help solving two biggest societal issues, reduction of CO_2 emissions and upcoming fuel crisis. Photocatalytic reduction of CO_2 is one of the most investigated reaction, nonetheless, major breakthrough is still required. The most investigated material in photocatalysis is titanium dioxide without any doubt. The major disadvantage of TiO_2 is the relatively wide band gap of approximately 3.2 eV. This means only UV irradiation can generate electrons and holes, however, the trend in photocatalysis is to utilize visible light.

Experimental/methodology. A series of TiO_2 photocatalysts was prepared by various methods resulting in different phase composition. TiHT was prepared using hydrothermal method from $TiOSO_4$ and NH_3. TiSG sample was prepared by sol-gel method from titanium isopropoxide.

Photocatalytic tests were performed in a batch stirred photoreactor. Reaction mixture contained 100 ml of 0.2M NaOH with a photocatalyst (0.1 g) and was saturated by He or CO_2. An 8W Hg lamp (λ_{max} = 254 nm) was used as the irradiation source. The gaseous samples were analyzed by a gas chromatograph (Shimadzu Tracera GC-2010Plus) equipped with BID (barrier discharge ionization detector). All of the measurements were reproducibly measured and three products were detected from photocatalytic reduction of CO_2 or during water splitting: H_2, CH_4 and CO.

Results and discussion. At pH = 7 the concentration of dissolved CO_2 (9744 mg/dm^3) is more than 100 times higher than at pH = 12.9 (84 mg/dm^3), but this fact is not crucial for the production of photocatalytic CO_2 reduction products. While higher CO yields were observed at pH = 7, the yields of CH_4 were higher at pH = 12.9. On the other hand, hydrogen generation is more than two times higher in case of photocatalytic reduction of CO_2 at pH = 7 (Fig.2).

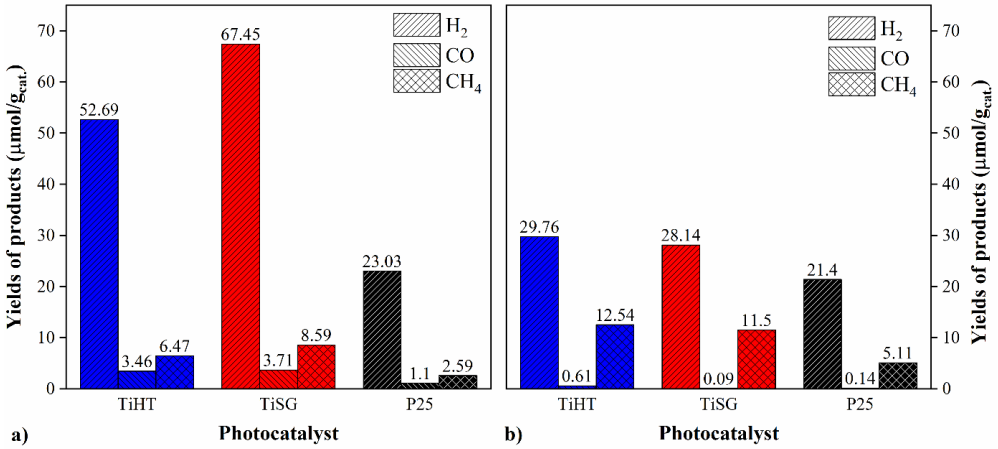

Figure 1: The results after 8 hours of 254 nm irradiation during photocatalytic reduction of CO_2 a) at pH = 7 and b) at pH = 12.9 over prepared TiO_2 photocatalysts and commercial TiO_2 P25.

Acknowledgments

The work was supported by ERDF "Institute of Environmental Technology – Excellent Research" (No. CZ.02.1.01/0.0/0.0/16_019/0000853), Large Research Infrastructure ENREGAT (project No. LM2023056), GA CR 21-24268K. The authors also thank the financial support provided by the Slovenian Research Agency (Grant Nos. N2-0188, P2-0273 and P1-0134).

A novel approach to fabricating a highly condensed oxygen-doped carbon nitride for wastewater treatment

Milad Jourshabani[1], Mahdieh Razi Asrami[1], Byeong–Kyu Lee[1*]

[1]*Department of Civil and Environment Engineering, University of Ulsan, Daehakro 93, Namgu, Ulsan, 44610, Republic of Korea*

[*]*Corresponding Author's E-mail: bklee@ulsan.ac.kr*

Keywords: Carbon nitride, Photocatalytic degradation, Wastewater treatment

Introduction. The presence of hazardous and nonbiodegradable organic compounds poses a potential risk to ecosystems and human health. Among the different technologies, visible light photocatalysis technology is an effective way to degrade a wide range of stubborn organic contaminants in wastewater. Recently, graphitic carbon nitride (CN) as a low-cost, simple, and metal-free photocatalyst with a visible light response has shown noticeable activities [1,2].

Experimental/methodology. In this study, a metal-free S-doped g-CN (S-g-CN) was obtained by thermal polycondensation of melamine, cyanuric acid, and thiourea; afterward, the sulfur-doped sites in S-g-CN were efficiently converted to C-O by simple calcination under a static air atmosphere without any additive. To monitor the photocatalytic performance of prepared O-doped g-CN was examined by degradation of RB and TC under visible light irradiation.

Results and discussion. The nanosheet characteristic of the as-prepared sample was studied by HRTEM; **Fig. 1a** shows the structure of g-CN, indicating an ultrathin nanosheet architecture that is favorable for light harvesting. Other characterization results prove that fabricated O-CN photocatalyst exhibits excellent visible light harvesting, charge carrier transition, and electronic properties (not shown here). In addition, it shows the highest electron density at the CB edge, which makes it a strong reduction photocatalyst. O-CN indicated excellent photocatalytic activity in the degradation of RhB (12 mg L^{-1}) and TC (12 mg L^{-1}) under visible light irradiation after 15 and 60 min, respectively (**Fig. 1b & c**).

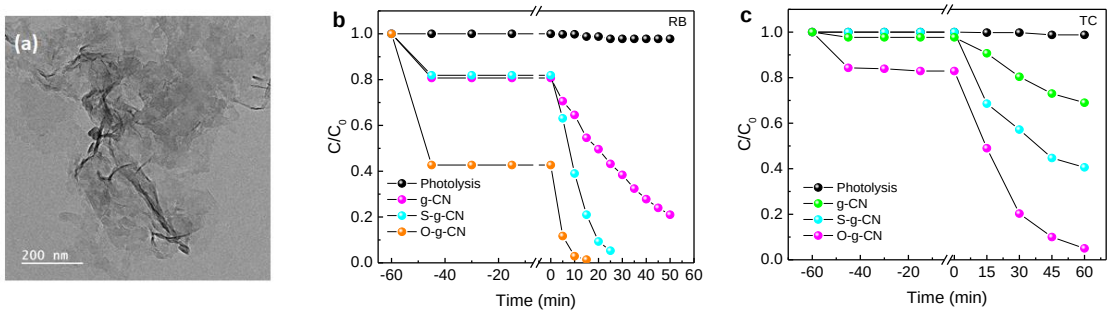

Figure 1. TEM image of g-CN; photocatalytic degradation of (b) RhB, and (c) TC for fabricated samples.

Acknowledgments

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Fe-based composites for the effective removal of wastewater pollutants

Arshitha Madhusudhan[1*], Thomas Roch[2], Martin Motola[1], Olivier Monfort[1]

[1]*Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University Bratislava, Slovakia.*

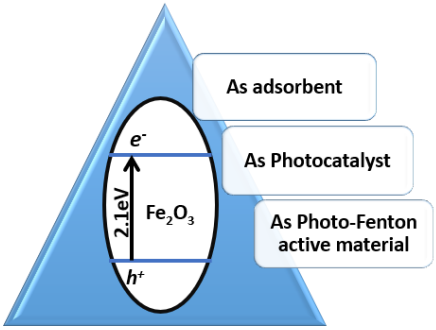
[2]*Department of Experimental Physics, Faculty of Mathematics Physics and Informatics, Comenius University Bratislava, Slovakia*.

m1@uniba.sk

Keywords: Adsorption, Photocatalysis, Fenton, Iron, Composites

Introduction: Fenton-based and photocatalytic processes are ones of the most widely studied Advanced Oxidation Processes (AOPs) to achieve wastewater treatment[1]. Fe-based composites have been widely used for this purpose due its cost efficiency, easy synthesis and efficient removal of pollutants[2]. In addition, pollutants such as carcinogenic dyes, hazardous pharmaceutical products are persistent, thus being seriously alarming concern for the environment[3]. Therefore, it appears crucial to understand how different AOPs can be synergistically combined along with adsorption in Fe-based composites, so more efficient wastewater treatments can be designed.

Methodology: Fe-based composite (containing a carbon-based adsorbent) is synthesized using hydrothermal method for efficient removal of a model pollutant. The synthesized catalyst properties are studied using XRD, DRS, and SEM while their efficiency is investigated along with assessment of adsorption, photocatalysis, and Fenton contributions. In addition, the role of radicals including •OH are also assessed.



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This work is partially supported by the Slovak Research and Development Agency under the contract No. APVV-21-0039, the Scientific Grant Agency of the Slovak republic (VEGA project No. 1/0319/23).

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Heterojunction semiconductors photocatalytic study

Ksenija Milošević, Davor Lončarević, Tihana Mudrinić, Jasmina Dostanić

Institute of Chemistry, Technology, and Metallurgy, Department for Catalysis and Chemical Engineering, University of Belgrade, Belgrade, 11000 Serbia

Keywords: photocatalysis, reaction mechanism, heterojunction, bandgap alignment

Introduction. Heterogeneous photocatalytic process has gained growing interest as an efficient method for environmental remediation and energy conversion by using a clean and renewable energy source. Photocatalysts are usually semiconductors that should fulfill key factors such as photogeneration of long-lifetime charge carriers, a suitable bandgap, a full range of sunlight utilization, sustainability, cost-effectiveness, high efficiency, and chemical and thermal stability [1]. To achieve these requirements, the main obstacles restricting efficient photoactivity, narrow light-response range and a high rate of charge carrier recombination, should be exceeded. Combining a semiconductor with a low valence band and a semiconductor with a high conduction band and adjusting a bandgap leads to the formation of heterojunction with improved charge separation, appropriate oxidation and reduction ability, and enhanced visible-light harvesting [2].

In our research, various binary heterojunction systems based on the wide-bandgap (TiO_2) and narrow-bandgap (g-C_3N_4, CuO, and Co_2O_3) photocatalysts were studied, with a thorough analysis of light harvesting, active species, and transport pathway of charge carriers, combined with the kinetics of the organic pollutants photodegradation.

Experimental/methodology. The morphological, optical, textural, and electrochemical properties of various photocatalysts were analyzed. The photocatalytic performance of the synthesized catalysts was tested in single and simultaneous systems using different organic pollutants.

Results and discussion. The synthesized photocatalysts displayed good adsorption capacity and enhanced visible-light photocatalytic performance in regard with neat photocatalyst. Formation of heterojunction between photocatalyst constituents brought to charge carriers transport pathway improvement and enhanced light harvesting. A radical scavenger study revealed the mechanism of interfacial interactions between photocatalyst constituents in single and multiple pollutant systems under solar and visible light irradiation, further indicating the type of heterojunction system (type II heterojunction or direct Z scheme). The type of heterojunction was found to be strongly influenced by the selection of combining photocatalyst constituents and their independent properties.

Acknowledgments

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Plasmonic Photocatalysts for Sustainable Artificial Photosynthesis.

Eva Naughton[a]*, Ravindranathan Thampi[b] and James A. Sullivan[a].

[a]*UCD School of Chemistry, Belfield, Dublin 4, Ireland.*
[b]*UCD School of Chemical and Bioprocess Engineering, Belfield, Dublin 4, Ireland.*
eva.naughton@ucdconnect.ie

Introduction: Since the industrial revolution fossil fuels have driven economic growth and now**,** approximately 85% of global energy generation comes from combustion of coal, oil, or natural gas [1]. However, temperature increases due to rising atmospheric CO_2 concentrations arising from their use are projected to have many negative impacts, and therefore scientists are looking for methods to remove excess CO_2. One method is the artificial photosynthesis (AP) reaction. Reacting CO_2 with H_2O to form CO or hydrocarbons using a sustainable energy source has become hugely desirable. The success of this process would contribute to the goal of creating a circular carbon economy and would ameliorate effects of fossil fuel use. Certain metals or conducting metal oxides can interact with UV or visible photons to give rise to a surface plasmon resonance, the oscillation of free electrons on the surface of a metal or metallic particle. These plasmons can decay *via* the generation of catalytically useful high energy "hot" electrons. Plasmonic nanostructures can act as co-catalysts with semiconductors, speeding up the transfer of excited electrons to acceptor molecules (either directly transferring "hot" electrons to an acceptor, or first injecting the electron into the CB of the semiconductor) and supressing exciton recombination, thereby increasing catalytic efficiency [2]. RuO_2, a plasmonic nanostructure, coupled with TiO_2, a UV-absorbing semiconductor, has shown to be active in the AP reaction, but neither component alone possessed the ability to both reduce CO_2 and oxidise H_2O under visible light irradiation [3]. In this study particles of RuO_2 were deposited on the surface of GaP (a CO_2 reducing catalyst) and Fe_2O_3 (a H_2O oxidising catalyst). The effect of the band edge positions of the semiconductors when coupled with RuO_2 in the AP reaction will be examined and used to help determine a mechanism of reaction.

Experimental: RuO_2, GaP, Fe_2O_3, and composites were prepared using hydrothermal syntheses. These were then characterised using XRD, FTIR, UV-Vis DRS, and CO_2-TPD. The presentation will also cover the reactivity of the materials in the AP reaction under batch conditions.

Results:

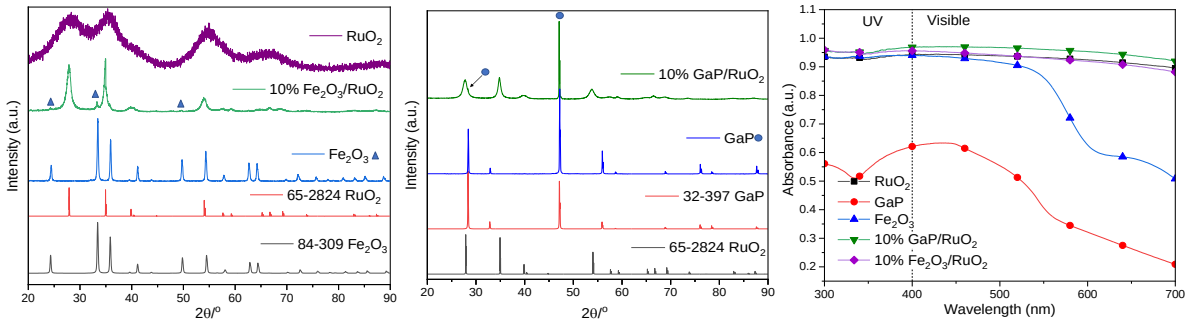

Fig. 1: XRD profiles (left and centre), and UV-Vis DRS spectra (right) of all prepared materials.

XRD shows GaP and Fe_2O_3 are present in the composites, providing a possibility for heterojunction formation at the relevant interfaces. As RuO_2 is a conductor, high absorbance values are observed across the UV-Vis spectrum. The composites' spectra show similar absorbance but also evidence of bandgaps in GaP and Fe_2O_3.

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2D-3D $Mo_{1.33}C$-TiO_2 composites for photocatalytic hydrogen production

M. Nair,[1] A. C. Iacoban,[1] A. Kuncser,[1] M. Florea,[1] F. Neațu,[1] A. Mininni,[2] H. Badr,[2] M. W. Barsoum,[2] Ş. Neațu[1*]

[1]*National Institute of Materials Physics, Magurele, Romania*
[2]*Department of Material Science and Engineering, Drexel University, Philadelphia, PA, USA*
[*]*stefan.neatu@infim.ro*

Introduction. Humanity is facing one of the largest energy crises and environmental pollution problems in history. It is commonly acknowledged that the usage of fossil fuels has caused the planet's temperature to rise in recent years, and the future seems bleak [1]. Photocatalysis, which converts solar energy into clean energy such as hydrogen, is one of the most effective approaches to overcome these challenges [2]. As photocatalysts, only a few semiconductors have been developed so far and no semiconductor possesses all of the qualities required for successful photocatalyst (visible light absorption, photostability, low cost, and abundance), hence many methods for improving semiconductor photocatalyst efficiency have been developed [3]. The coupling of a suitable and powerful photon absorber (the semiconductor photocatalyst) with a material with high metallic conductivity (such as *i*-MXene) to perform the reaction at high conversions is thought to be an effective way of developing robust, safe, cost-effective, and efficient photocatalytic systems for water splitting [4]. Finding the right combination is difficult, but in this research line, the current study aims to develop *i*-MXene-based composites for photocatalytic hydrogen production.
Experimental/methodology. Several $Mo_{1.33}C/TiO_2$ composite materials were effectively produced in this study using an *in situ* solvothermal technique. The $Mo_{2/3}Y_{1/3}AlC$ *i*-MAX phase was used as a starting material for a chemical transformation that resulted in $Mo_{1.33}C$ *i*-MXene. This synthesis was carried out using numerous overextraction techniques with different synthesis parameters (reaction duration, HF solution concentration, etc.). This $Mo_{1.33}C$ *i*-MXene was then combined with TiO_2 nanoparticles to produce a composite material that exhibited improved photocatalytic activity. The phocatalytic studies were carried out in a cylindrical quartz reactor containing either MilliQ water (with no hole scavenger) or a water-methanol mixture (volumetric ratio of 4:1). A heatless illumination Xe light lamp system (MAX-303 from Asahi Spectra equipped with a UV-Vis (300-600 nm) mirror module) was employed as an irradiation source. In order to characterize these composites both before and after the reaction, a number of different techniques, including XRD, TEM, XPS, UV-Vis and Raman spectroscopies, were utilized in this study.
Results and discussion. The hydrogen production rates and the obtained apparent quantum yields (AQY) calculated at 365 nm are shown in Table 1. As seen, under specific experimental conditions, the best photocatalyst generates a hydrogen production rate of more than 1.2 mmols/gh.

Table 1 The obtained hydrogen production rates under UV-Vis light irradiation

Photocatalysts	AQY (%)	H_2 production rate (µmol/gh)
0% $Mo_{1.33}C/TiO_2$	4.20	772
1% $Mo_{1.33}C/TiO_2$	4.88	897
3%-$M_{1.33}C/TiO_2$	5.56	1022
5% $Mo_{1.33}C/TiO_2$	6.81	1252

The obtained values are among the highest for *i*-MXene-based photocatalysts. The discoveries give up new possibilities for the creation of highly active noble metal-free materials for photocatalytic H_2 production.

Acknowledgments
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Preparation of Carbon Dots (CDs) from Coconut Water and CDs/ZnO composite Photocatalyst for Degredation Reactive Red 141 Azo Dye.

David Nugroho[1], Suwat Nanan[2] and Rachadaporn Benchawattananon [1,*]

[1]*Department of Integrated Science, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand; davidnugraha95@gmail.com*
[2]*Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand.*
**Correspondence: rachadaporn@kku.ac.th (R.B.)*

Keywords: Carbon dots, Zinc Oxide, Nanoparticle, Photocatalyst, RR141 Dye

Introduction. Reactive Red 141 are the commercial names of the dye. Its empirical formula is $C_{52}H_{22}Na_8O_{26}S_8Cl_2N_{14}$ and is composed of two monochlorotriazine reactive groups. Reactive Red 141 (RR141) is a sulfonated, bright red color diazo reactive textile dye and is widely used for the dyeing processes in the textile industry. Sulfonated azo dyes have a negative aesthetic effect on the wastewater that is highly colored even at a low concentration of dye. The removal of the dye in natural water is urgently needed.

Experimental / methodology : Carbon dots (CDs) has been synthesis by hydrothermal mehod using the temperature of 180 °C for 4 hours from Coconut water. After that the CDs was mixed with ZnO for preparation of the composite using two different methods namly the hydrothermal and the precipitation methods. The sample was dried in the oven to become powder. The CDs/ZnO has been applied for removal of RR141 dye solution in wastewater.

Result and Discussion : The UV-light-driven photodegradation of reactive red 141 (RR141) by using the prpared photocatalyst was investigated.The lowering of RR141 concentration in the presence of with CDs/ZnO was found. The CDs/ZnO composite obtained from hydrothermal method showed higher performance than those obatied from bare CDs and CDs/ZnO composite obtained from precipiation method. The highest efficincy of about 90% was achieved with the greatest rate constant of about 0.020 min^{-1}. The degradation of other pollutants is under investigation. The recycling ability of the sample will be determined.



Figure 1. Scheme Synthesis of N-CDS and the application.

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Development of photocatalytic filters for the degradation of indoor air pollutants

I. M. Oliveira[1*] and J. P. S. Sousa[2]

[1]*International Iberian Nanotechnology Laboratory (INL), Avenida Mestre José Veiga s/n, 4715−330, Braga, Portugal*

[2]*International Iberian Nanotechnology Laboratory (INL), Avenida Mestre José Veiga s/n, 4715−330, Braga, Portugal*

[*] *Isabel Matos Oliveira- isabel.oliveira@inl.int*

Introduction.

Most people spend between 70 to 90% of their time indoors. Additionally, many pollutants found in outdoor air are found in indoor air but at higher concentrations than outdoors. Indoor air quality problems of greatest concern at present are: passive exposure to tobacco smoke, formaldehyde exposure, nitrogen dioxide from gas-fuel cooking stoves, radon daughter exposure, and the diverse health problems encountered by workers in newer sealed office buildings [1]. Unlike other air purifiers which mostly trap particulate matter, photocatalysis is a promising new technology that can convert these indoor air pollutants into non-harmful products. For this purpose, an efficient composite photocatalyst, nitrogen (N) doped TiO_2/graphene oxide (GO) has been synthesized. TiO_2 nanoparticles are generally believed to be the most promising photocatalysts because of their non-toxicity, cheapness, long-term stability and high reactivity. Generally, there are three main approaches to improving the photocatalytic activity of TiO_2: band-gap tuning, minimizing charge carrier recombination, and absorbance of reactants on the surface of photocatalysts thereby promoting the forward reaction [2]. Nitrogen (N) doping shifts the valence band edge of TiO_2 and the combination of GO with TiO_2 serves the other two approaches of minimizing charge carrier recombination and absorbance of reactants. The increase in visible light activity was proposed by the creation of a sub-band level N2p orbital instead of the O2p orbital by nitrogen doping, thereby shifting the valence band edge. It was experimentally confirmed that the material has visible light activity. Graphene oxide has a 2D geometry that allows for excellent electron-transport properties and has a photoelectron reservoir due to its high conductivity. The photo-generated electrons from a TiO_2/graphene oxide interface can be more successfully accepted, stored and utilized in a redox reaction. The decreased electron–hole recombination and extended lifetime of electrons resulting from their separation are proposed as the key factor for improving the photocatalytic performance of TiO_2/graphene nanocomposites.

Experimental/methodology.

The commercial nanomaterials (titanium P25 and graphene oxide) were functionalized with different nitrogen and boron precursors. The nanocomposites were prepared using two approaches: (1) simple mixing and (a) with hydrazine hydrate. The prepared materials were characterized by complementary techniques. In order to do a screening of the catalytic activity of the materials it was performed photocatalytic experiments in water using a standard organic dye. The materials in powder form were immobilized in the support by different techniques: Wet infiltration, Dip coating and Spray coating.

Results and discussion. The material that present the best photocatalytic activity was the composite material (N-titanium dioxide/GO). A coating technique has been developed, having good photocatalytic activity and adhering well to the surface of the substrate. Even after 4 days of continuous operation, no material was removed from the support, it shows the robustness of the coating.

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Investigating the Photocatalytic Performance and Kinetics of Commercial TiO_2-P25 and ZnO Nanoparticles for Ibuprofen Photodegradation.

Maryam Hmoudah[1,2*], Carmela Chianese[1], Vincenzo Russo[1,2], Martino Di Serio[1], Tapio Salmi[2]

[1]*Department of Chemical Sciences, University of Naples Federico II, Naples, Italy*
[2]*Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku/Åbo*

**** Correspondence: Maryam Hmoudah, maryam.hmoudah@abo.fi***

Keywords: *zinc oxide, titanium dioxide, nanoparticles, ibuprofen, photodegradation, kinetics, thermodynamics.*

Abstract:
In this study, the photocatalytic activity, reaction kinetics, thermodynamics and modeling of commercial TiO_2-P25 and ZnO nanoparticles (NPs) for ibuprofen (IBU) photodegradation were examined using a batch reactor under ultraviolet (UV) irradiation. The reaction kinetics was modeled using first and second order rate equations, and the reaction mechanisms were identified. The photodegradation performance of both TiO_2 and ZnO NPs was further studied under varying reaction conditions including temperature (as shown in Figure 1), catalyst bulk density, and initial IBU concentration. The chemical and physical-diffusive aspects of the reaction were analyzed and the goodness of the kinetic models was evaluated. The results showed that the reaction rate for TiO_2 was of first order, while ZnO NPs followed second order kinetics with respect to IBU. The photodegradation mechanisms for TiO_2 and ZnO NPs were determined to be Langmuir-Hinshelwood and Eley-Rideal type, respectively. The thermodynamic parameters, including Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were assessed, indicating efficient photodegradation performance by these NPs. The reaction kinetics, mechanism, and model consistency with parameters combined with experimental data validation will be elaborated and discussed further during the presentation.

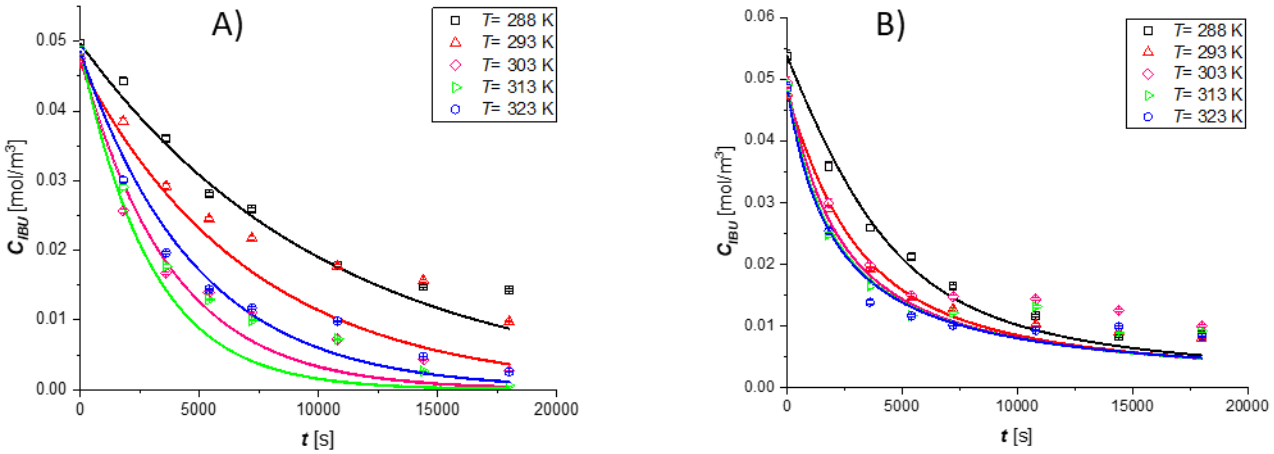


Figure 1. Experimental results of the kinetic tests conducted at different temperatures. $C_{IBU,0}$ = 4·10^{-2} mol/m^3, ρ_B = 0.5 kg/m^3, Q_{air} = 0.94·10^{-6} m^3/s and v = 750 rpm. Trends of the concentration profiles *vs* the reaction time for A) TiO_2 and B) ZnO.

Impact of the strength of Pd-perovskite interaction in Natural Gas Vehicle three-way catalysts: A kinetic approach

Y. Zheng, F. Dhainaut,. P. Granger*

Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

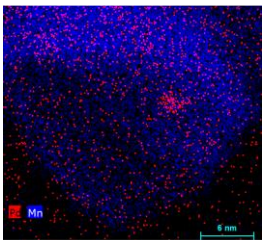
Keywords: Natural Vehicle Catalyst, CH_4 combustion, perovskite, palladium

Introduction.

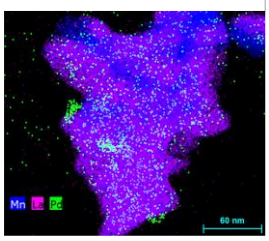
Natural gas fuelled engines are an alternative to gasoline and diesel engines less pollutant with emission particulate almost nil and lower greenhouse gas and NO_x emissions. However, the complete removal of residual traces of methane, acting as greenhouse gas, remains an important challenge. The complete removal of CH_4 induces the installation of palladium-based Three-Way-Catalyst (TWC) running at higher temperature to activate methane. Highly loaded palladium catalysts can be developed to insure an acceptable conversion at moderate temperature and slow down detrimental effects of deactivation. An alternative consists in optimizing the nature of interaction between Pd and support exhibiting oxygen storage properties in order to create synergistic effects on the catalyst activity. Different methods, *e.g.* sequential vs. on pot methods, were implemented for the introduction of palladium onto the surface of $LaMnO_3$ perovskite support or inside the perovskite lattice respectively. The kinetics of methane combustion has been investigated on freshly-prepared samples and on aged samples at 750°C in wet conditions in order to understand the implication of the Pd-support interface on the kinetics, to evaluate the impact of subsequent deterioration induced by thermal ageing and/or water accumulation at the surface.

Results and discussion.

One pot method



Sequential method



TEM analysis revealed in all cases well-dispersed cationic Pd^{n+} species predominantly stabilized in octahedral coordination of $LaMnO_3$ lattice according to a on pot method. In contrast, successive wet impregnation of the perovskite led to significant aggregation of palladium particles (look at the figures opposite). Aging in the presence of 10 vol.% H_2O in air induced partial exsolution of palladium on the one pot sample which lead to the creation of strong interaction at the surface of $LaMnO_3$ avoiding extensive particle sintering. In contrast, PdO aggregates originally dispersed through impregnation weakly interact with the support and was found more sensitive to thermal sintering.

Kinetic measurements in the absence of water showed that the Pd-support interaction will govern the kinetics and can be related to a dual site mechanism which combines Pd and reactive oxygen species from the support. Such reaction mechanism has been compared especially on aged samples to a single site reaction mechanism involving only palladium. Based on this it was foung that significant particle Pd sintering on impregnation detriorates the interface and leads to a partial restoration of the single site mechanism whereas the dual site mechanism runs on the aged one pot sample.

Interestingly, further comparisons of both mechanisms when the reaction is performed in wet conditions show the suppression of the dual site mechanism irrespective of the method used for palladium deposition. Such changes have been explained by water hydrolysis of surface reactive oxygen species stabilizing into unreactive OH species. As a consequence, the Pd-support is deteriorated. A quantitative analysis based on the estimation of thermodynamic and kinetic parameter allow more extensive discussion especially on the adsorptive properties of Pd sites also perturbated.

Palladium doped reduced graphene oxide-TiO_2 composites for enhanced visible-LED photocatalytic erythromycin degradation

Luisa M. Pastrana-Martínez[1], Lucía Rossi[2], Sergio Morales-Torres[1], Paula I. Villabrille[2], Janina A. Rosso[3], Francisco J. Maldonado-Hódar[1]

[1]*NanoTech-Nanomaterials and Sustainable Chemical Technologies. Department of Inorganic Chemistry. Faculty of Sciences. University of Granada. Avda. Fuente Nueva s/n, 18071, Granada. Spain.*
[2]*Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. Jorge J. Ronco" (CINDECA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CCT La Plata–CONICET, La Plata, Argentina.*
[3]*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CCT La Plata–CONICET, La Plata, Argentina.*
**lpastrana@ugr.es*

Introduction. Heterogenous photocatalysis has demonstrated to be a promising option in water treatment, while nanotechnology opens a gate for the development of high-efficient and stable photocatalysts. Different carbon materials have been used to prepare TiO_2-based photocatalysts with enhanced catalytic properties, as well as noble metals (e.g., Ag, Au, Pt, Pd) acted as electron trapping sites promoting interfacial charge transfer processes in the resulting composites. In particular, the use of composites based on nanostructured TiO_2 and graphene oxide (GO) or reduced graphene oxide (rGO) is an interesting topic of research in photocatalysis, because an enhancement of the properties of the materials is expected to occur, due to a synergic interaction between both phases at the nanoscale [1,2] as well as to provide anchoring sites for noble-metal particles.

Experimental/methodology. Pd-doped rGO-TiO_2 composites were prepared by the sol-gel process and subsequently different post-treatments, such as thermal treatment in N_2 atmosphere and hydrothermal treatment were also carried out. The effect of the synthesis conditions on the properties of each material was studied and its photocatalytic activity was evaluated for the degradation of 10 mg L^{-1} erythromycin A (Ery-A) solution under two different irradiation sources: simulated solarbox (SB) and a Solar-LED. Different aliquots were withdrawn, filtered and analyzed by UPLC-MS to determine the concentration of pollutant removed.

Results and discussion. The rGO-TiO_2 composites presented a good dispersion of the palladium on the material surface, even so a very small amount of metal (0.1 wt.%) was deposited. Pd nanoparticles were ranging 1-2 nm and a larger dispersion was achieved when rGO-TiO_2 was used as support in comparison with only TiO_2. XRD patterns exhibited the typical peaks associated to the anatase phase for all composites, but no signals were detected for Pd, which could be explained to their very small Pd-particle size. The materials obtained presented small values of BET surface area but considerable mesoporous volumes, which is very important for water treatment applications. Furthermore, the Pd-rGO-TiO_2 composites presented a narrowing band gap compared with the reference materials without Pd or rGO. The activity of the photocatalyst was determined by the different pre-treatment carried out and the type of irradiation source used. Thus, composites prepared by sol-gel method followed by a hydrothermal treatment achieved the total Ery-A degradation for 120 min under solar irradiation, while that prepared with thermal treatment achieved a Ery-A degradation of around 80 %. The activity of both materials was lower when a LED-visible was used, only a 50% being achieved at 300 min for Pd-rGO-TiO_2.

Acknowledgments

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Nanostructured ferrites as possible catalyst for plasmon – assisted N_2 photofixation

Lorenzo Rizzato[1*], Antonella Glisenti[1,2]

[1]*Department of Chemical Sciences, University of Padova, Via Marzolo 1, Padova, 35131, Italy*
[2]*ICMATE - Department of Chemical Sciences, University of Padova, Via F. Marzolo 1, Padova, 35131, Italy*
[*]*lorenzo.rizzato.1@phd.unipd.it*

Keywords: photocatalysis, N_2 fixation, plasmonics, perovskites

Introduction

Amonia is proven to be one f the most synthetised chemicals in the world, having application in different fields, from pharmaceutical to agricolture; however, high temperatures and pressures (400 – 500 °C and 150 atm) make the Haber Bosch process rather energy – intensive and responsible for 3% of CO_2 global emissions [1]. Thus, finding new ways of producing ammonia in milder conditions is crucial to ensure a sustainable future. Plasmonic photocatalysis has proven to be a promising research field, as it benefits from localized surface plasmon resonance (LSPR); indeed, the collective movement of electrons can cause effective charge separation and accumulation, thus enhancing the catalytic performances. For this reason, catalyst design is crucial to ensure good light absorption, charge separation and N_2 activation [2]; perovskite – based materials are promising candidates for nitrogen fixation reaction, as for their tunability of structural, electronic, and functional properties [3]. Herein, we report $La_{0.9}Fe_{0.9}Cu_{0.1}O_3$ and $La_{0.9}Fe_{0.9}Ni_{0.1}O_3$ as possible systems for the plasmonic – assisted NH_3 synthesis using a commercial 100 W LED.

Experimental/methodology

$La_{0.9}Fe_{0.9}O_3$ and $La_{0.9}Fe_{0.9}Cu_{0.1}O_3$ and $La_{0.9}Fe_{0.9}Ni_{0.1}O_3$ were synthetized through a sol gel method, using metal nitrates as precursors and citric acid as complexing agent. Surface decoration was achieved through an exsolution process, treating Cu- and Ni-doped catalysts in 5%H_2/Ar at various temperatures and times. Structural analysis was achieved by means of XRD; morphological properties were probed using SEM and energy – dispersed X-ray spectrometry (EDX), while surface composition was observed through XPS. Specific surface area was evaluated using BET analysis; temperature programmed reduction (TPR) and desorption (TPD) were used to gain information about the active species and the adsorption properties of the catalysts. Catalytic tests were performed exposing 50 mg of catalyst to a 100 cm^3/min flux containing 2% N_2 and 6% H_2; a cost-effective, scalable approach was undertaken, using commercial 100 W LED lamp for 1 h to illuminate the system.

Results and discussion

Structural analysis pointed out that only the perovskitic phase was formed during the synthetic process, with no evidence of Fe impurities or Cu and Ni oxides; after the exsolution treatment, reflections of metallic Cu and Ni were observed in $La_{0.9}Fe_{0.9}Cu_{0.1}O_3$ and $La_{0.9}Fe_{0.9}Ni_{0.1}O_3$, respectively. A ≈10 m^2/g surface area was obtained for all the samples, with slight variations due to the insertion of dopants in the structure. XPS analysis confirmed the surface enrichment of Cu and Ni after exsolution; nanoparticles were observed during SEM measurements. Promising results were obtained in the catalytic reduction of nitrogen with hydrogen, achieving a good conversion at RT. Different conversions were observed at different temperatures, suggesting that more than one reaction mechanism may take place, depending on the electron excitation pathway. LSPR contribution to the catalytic activation of nitrogen was evaluated combining UV-VIS spectroscopy and the catalytic characterization.

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H_2 Production from the Photocatalytic Reforming of Ethylene Glycol

L. Roebuck[1*], H. Daly[1], C. Hardacre[1]

[1]*University of Manchester, Manchester, United Kingdom*
[*]*luke.roebuck@postgrad.manchester.ac.uk*

Keywords: Photocatalysis, Hydrogen, Ethylene Glycol, ATR-FTIR

Introduction.

Photocatalytic reforming (Photoreforming) for the production of H_2 has become an area of much interest in recent years due to it's potential for the production of clean hydrogen from either biomass or waste/pollutant sources by solar irradiation [1]. Photoreforming makes use of a photocatalyst for the conversion of an organic substrate and water into H_2 and CO_2. Organic substrates studied include lignocellulosic biomass, plastics, sugars, and alcohols among others. The reaction mechanisms however are complex and not well understood. In this work the photoreforming of ethylene glycol and propylene glycol are investigated. These molecules are interesting in themselves as they are present as pollutants and as waste materials in some industrial processes. However, as relatively simple molecules, their study also serves as a tool to better understand the fundamental reaction mechanisms in photoreforming for more complex substrates.

Experimental/methodology.

Pt/TiO_2 catalysts were prepared using the incipient wetness impregnation method. Photoreforming experiments were performed in an 80ml quartz reactor irradiated using a UV(λ=385nm) LED array. The reactions were performed under a constant flow of Ar gas which was also used to carry gaseous products for analysis by gas chromatography. Liquid phase products were analyzed post-reaction using HPLC. The adsorption of reactants and their surface reactions were investigated by in-situ using ATR-FTIR spectroscopy.

Results and discussion.

It was found that the TiO_2 polymorph used in Pt/TiO_2 photocatalysts has a significant effect on the photoreforming of ethylene glycol under UV irradiation. The anatase polymorph was found to produce more hydrogen than either rutile or mixed anatase:rutile phases. This is in contrast to much of the photocatalytic literature where mixed phase titania is preferred due to its enhanced separation of photogenerated charge carriers [2]. This effect was explained by a change in the reaction mechanism when even only small quantities of rutile phase is present in the photocatalyst. In Pt/anatase catalysts the major oxidation mechanism proceeds initially via the abstraction of α-hydrogens by radical species. On the other hand, in rutile or mixed phase catalysts, dissociative adsorption of the hydroxyl groups to form alkoxy intermediates is favoured. This mechanism leads to the formation of formaldehyde that accumulates in the liquid phase and prevents full oxidation to CO_2. Further work on propane-1,2-diol and propande-1,3-diol is ongoing to further probe this effect. Furthermore, it was found that surface-bound dicarboxylic acids such as terephthalic acid further enhances the hydrogen production and substrate conversion. Preliminary investigation indicates that water splitting is promoted by the free acid group of the terephthalic acid which aids proton transfer.

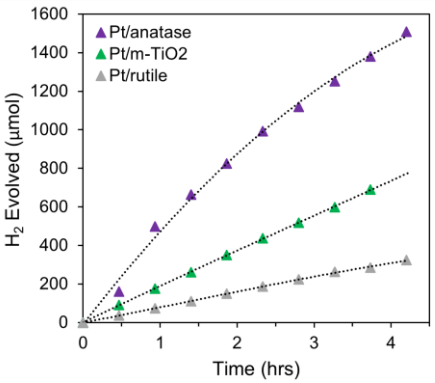

Figure 1: Hydrogen evolution from the photoreforming of 0.3M ethylene glycol using Pt/TiO_2 photocatalysts with different TiO_2 polymorphs

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Changes in photocatalytic behavior of g-C_3N_4/TiO_2 composites with varying the morphology of TiO_2

M. Roškarič[1*], G. Žerjav[1], J. Zavašnik[2], A. Pintar[1]

[1]*National Institute of Chemistry, Ljubljana, Slovenia*
[2]*Jožef Stefan Institute, Ljubljana, Slovenia*
[*]*matevz.roskaric@ki.si*

Keywords: g-C_3N_4/TiO_2 photocatalysts, TiO_2 morphologies, heterogeneous photocatalysis, bisphenol A degradation, visible-light irradiation

Introduction. Heterogeneous photocatalysis is a hot topic in the field of waste-water remediation, because light of an appropriate energy can be utilized for the oxidative mineralization of water-dissolved organic pollutants [1]. The most commonly used photocatalyst, titanium dioxide (TiO_2), has two major drawbacks: (i) a wide band gap value (E_{BG}=3.0-3.2 eV), and (ii) high rate of the electron-hole pair recombination [2]. These drawbacks of TiO_2 can be overcome by using different TiO_2 polymorphs [2], doping TiO_2 with metals [3], depositing noble metals on TiO_2 surface [3], or combining TiO_2 with low band gap organic semiconductors like graphitic carbon nitride (g-C_3N_4, E_{BG}=2.6-2.7 eV, S_{BET}=16 m^2/g) [1], etc. Therefore, the aim of this study was to synthesize g-C_3N_4/TiO_2 composites using different TiO_2 morphologies and to study the influence of the selected TiO_2 morphology onto the electronic, optical and photocatalytic properties of the synthesized g-C_3N_4/TiO_2 composites.

Experimental/methodology. The synthesis of g-C_3N_4 from dicyandiamide was carried out as follows: end temperature 550°C, 300 °C/h, and 4 hours in air in a muffle furnace. Commercially available TiO_2 nanoparticles (DT-51, CristalACTiV™) represent the spherical-like TiO_2 (TNS) and were further used for the synthesis of amorphous TiO_2 nanorods (aTNR) by the synthesis procedure described in [2]. The crystalline TiO_2 nanorods (TNR) were obtained by the annealing of aTNR at 500 °C (120 °C/h) for 2 hours in air. For the formation of g-C_3N_4/TiO_2 composites, TiO_2 particles of different morphologies and g-C_3N_4 in a weight ratio 1:1 were ground in an agate mortar. The catalysts were denoted as g-C_3N_4/TNS (S_{BET}=57 m^2/g), g-C_3N_4/aTNR (S_{BET}=164 m^2/g) and g-C_3N_4/TNR (S_{BET}=57 m^2/g).

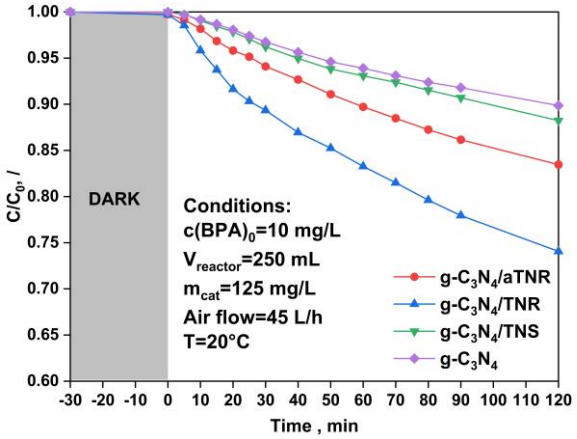

Figure 1. Photocatalytic degradation of aqueous BPA solution conducted in the presence of investigated catalysts under visible-light illumination.

Results and discussion. Combining TiO_2 and g-C_3N_4 significantly improved the initial low specific surface area of g-C_3N_4 and prolonged the "life-time" of charge carriers due to the injection of photogenerated electron from conduction band (CB) of g-C_3N_4 to CB of TiO_2. Additionally, the presence of g-C_3N_4 enables the utilization of visible light by the g-C_3N_4/TiO_2 composites for the charge carrier generation. From the results of photocatalytic oxidation runs of aqueous solution of bisphenol A (BPA) illustrated in Fig. 1, we can conclude that the g-C_3N_4/TNR composite exhibited the highest visible-light triggered photocatalytic activity toward the BPA degradation, which is due to the optimal balance between the specific surface area, the crystallinity of the selected TiO_2 morphology and optimal formation of the g-C_3N_4/TiO_2 heterojunction.

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Sono-photo hybrid catalytic process for the degradation of Tetracycline

S. Sajjadi and R. Klement

Dept. of Functional Materials, FunGlass, Alexander Dubček University of Trenčín, Študentská 2, 911 50 Trenčín, Slovakia

Keywords: Core-shell catalyst; Advanced oxidation processes; Bismuth tungstate; Indium sulfide; Tetracycline.

Introduction. Recently, combinations of various advanced oxidation processes (AOPs) have been applied to treat detrimental compounds from wastewater. Sonophotocatalysis can manifest the high degradation of a broad domain of contaminants [1]. Bismuth tungstate (Bi_2WO_6) is an n-type, narrow band gap (2.8–3.0 eV) semiconductor and has been considered a hopeful catalyst. Despite its high photocatalytic activity, pristine Bi_2WO_6 is not ideal due to photo-induced charge rapid recombination [2]. The indium sulfide (In_2S_3) semiconductor possesses a narrow band gap (1.8–2.3 eV), excellent visible light response, and a negative conduction band (CB) edge. However, its relatively slow carrier separation and migration kinetics make its catalytic performance unsatisfactory [3]. Additionally, magnetic supports could overcome the limitation of separation from the liquid phase, thus the catalyst could be effectively recycled by applying an external magnetic field [4]. Hence, in this study, the Z-scheme $In_2S_3/Bi_2WO_6/Fe_3O_4$ magnetic core-shell structure catalyst was prepared for the sonophotocatalytic degradation of tetracycline (TC).

Experimental. In_2S_3 microspheres, Bi_2WO_6 nanosheets, and In_2S_3/Bi_2WO_6 core-shell structures were prepared by the hydrothermal method. In_2S_3/Bi_2WO_6 core-shell structures were decorated with Fe_3O_4 by the co-precipitation method to achieve an $In_2S_3/Bi_2WO_6/Fe_3O_4$ magnetic core-shell catalyst. The prepared catalyst was characterized by SEM, EDX, DRS, XPS, and BET. In addition, the catalytic activity of the $In_2S_3/Bi_2WO_6/Fe_3O_4$ catalyst was investigated by sonophotocatalytic degradation of TC.

Results and discussion. The effects of $In_2S_3/Bi_2WO_6/Fe_3O_4$ and its components on the degradation efficiency of TC through sonophotocatalytic processes are shown in Figure 1. The 0.5 g/L of $In_2S_3/Bi_2WO_6/Fe_3O_4$ in solution with pH=6.5 and TC (10 mg/L) showed a high degradation efficiency of TC (94.7% within 60 min), under visible LED light (50 W) and ultrasound irradiation (140 W). This high catalytic activity of the $In_2S_3/Bi_2WO_6/Fe_3O_4$ core-shell catalyst was mainly attributed to the synergistic effects of the formed interfaces between the shell and core, which generate an electric field to facilitate charge transfer. Additionally, direct Z-scheme heterojunction inhibits e^- and h^+ charge recombination and expands light absorption in the visible range. Furthermore, the results expressed the presence of synergy between the combined systems (sonocatalysis and photocatalysis). $In_2S_3/Bi_2WO_6/Fe_3O_4$ showed good reusability and stability.

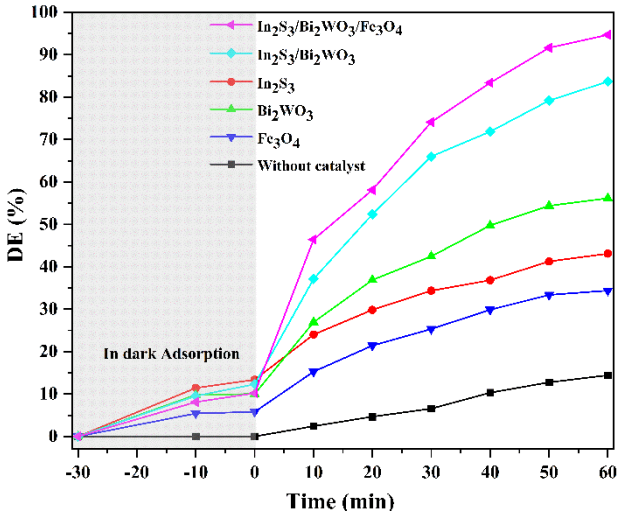

Figure 1. The degradation of TC in the presence of $In_2S_3/Bi_2WO_6/Fe_3O_4$ and its components

Acknowledgment

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Synergistic Effect of Bismuth and Molybdenum-Based Heterojunction Photocatalysts with Peroxymonosulfate for Efficient Degradation of N-Methyl-2-Pyrrolidone

P. Kumar[1], S. Verma[2*], U. L. Stangar[1]

[1] *Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia*
[2] *School of Energy & Environment, Thapar Institute of Engineering & Technology, Patiala-147004, Punjab*
**Corresponding Author's E-mail address – shilpi.verma@thapar.edu*

Keywords: Bismuth/ molybdenum based photocatalyst, NMP, band gap, sulfate radical, PMS

Introduction. N-Methyl-2-pyrrolidone (NMP) is a cyclic amide that poses risks to human health, including impacts on the reproductive, liver, kidney, immunological, developmental, and central neurological systems (Li et al., 2018; Web reference-1). Therefore it is imperative to effectively remove the NMP from the water. Advanced oxidation processes (AOPs) offer a promising solution for the degradation of NMP. By forming heterojunction structures with semiconductors or metals, photocatalyst's activity can be significantly improved through increased charge separation, charge transfer, and lifespan of charge carriers (Hojamberdiev et al., 2013). This study investigates the use of bismuth (Bi) and molybdenum (Mo) based photocatalysts with peroxymonosulfate (PMS) for the efficient degradation of NMP.

Experimental/methodology. A modified hydrothermal technique was used to prepare the heterojunction Bi_2MoO_6 photocatalyst with varying bismuth amounts. The synthesized photocatalysts were characterized for structural and spectral characteristics using various techniques such as XRD, PL, SEM-EDX, UV-DRS and FT-IR. The NMP was degraded in a specially built photoreactor chamber during The photocatalytic studies. The NMP had an initial concentration of 10 mg/L, while the catalyst had a 15 mg/L concentration. Irradiation was performed with a set of three lamps (Philips) with an emission wavelength of 365 nm, arranged radially around the reactor. PMS was added to the reaction mixture with varying concentrations. A 100 µL sample was drawn using a syringe filter into an HPLC vial at a specified fluence interval, and 1mL methanol (HPLC grade) was added as a quencher. Initially, the experiments were conducted with only NMP and photocatalysts in the dark to observe the effect of UV irradiation.

Results and discussion. Well crystalline structure of the photocatalyst was observed through XRD. UV-DRS analysis showed that the synthesized photocatalyst was activated in UV-A spectral range. Negligible NMP degradation was observed under UV irradiation. With the addition of Bi2MoO6 photocatalyst under UV-irradiation, the degradation was improved to 45%. The addition of PMS in this reaction mixture significantly enhanced the NMP degradation to more than 90%. However, as the concentration of NMP was increased, the degradation was found to be reduced. This resulted because the radicals generated during the reaction was quenched by the intermediates and by-products formed during the degradation process. The various components of the water matrix had different effects on the degradation of NMP; some components improved the degradation, while others reduced the degradation of NMP.

Acknowledgments

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Synthesis and characterization of Au/TiO_2 catalysts with different loadings of Au for heterogeneous photocatalysis

Š. Slapničar[1*], G. Žerjav[1], A. Pintar[1]

[1]*National Institute of Chemistry, Ljubljana, Slovenia*
[*]*spela.slapnicar@ki.si*

Keywords: titanium dioxide, heterogeneous photocatalysis, gold nanoparticles, plasmonic metals

Introduction. The focus of research work in the field of heterogeneous photocatalyis for waste water treatment lies in the utilization of the semiconducting titanium dioxide (TiO_2) as the photocatalyst. The results show that TiO_2 is one of the best and versatile materials for photocatalysis, but it has a drawback of a wide band gap (3.2 eV). This can be overcome, for instance, by depositing plasmonic metal nanoparticles (e.g., Au) onto the surface of TiO_2, which in turn would enable harvesting of visible light and near-infrared radiation of the solar-light spectrum. Au/TiO_2 catalysts exhibit a strong visible-light absorption band at 500-600 nm due to the localized surface plasmon resonance (LSPR) effect exerted by Au particles [1,2]. Therefore, the aim of the present work was to synthesize Au/TiO_2 catalysts with different Au loadings and to investigate in detail their optical, electronic and morphological properties as well as to link them with their efficiency in generation of different reactive oxygen species (ROS).

Experimental/methodology. In the presented work, we used TiO_2 in the form of nanorods (TNR) prepared by hydrothermal synthesis procedure [1], onto which different weight loadings of Au nanoparticles (0.1, 0.4, 0.7 and 1.0 wt.%) were deposited by using the wet impregnation technique. The mixture was stirred for 21 hours, then dried at 80 °C and the obtained materials were calcined at 300 °C [3]. To evaluate the photocatalytic activity of investigated Au/TiO_2 catalysts, we performed a series of experiments to determine the oxidation pathway of the water-dissolved model organic pollutant bisphenol A (BPA). We further performed tests with 2,2-diphenyl-1-picrylhydrazyl (DPPH), 2,2´-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid cation ($ABTS^{\bullet+}$) and coumarin (COUM), acting as radical scavengers, to measure the visible-light triggered generation rates of different ROS (i.e. superoxide anion and $OH^{\bullet}$ radicals).

Results and discussion. The results of SEM-EDX analysis show that the actual Au loading is the same as the nominal one in all investigated Au/TiO_2 catalysts. N_2 physisorption analysis revealed that the specific surface area, pore volume and pore diameter did not change after Au impregnation on TNR, which means that Au ensembles did not block the pores of TNR. The UV-Vis DR spectra of all prepared Au/TiO_2 catalysts show an absorption of light in the UV-light region (below 400 nm) due to the presence of TiO_2, and an absorption peak (hump) at around 550 nm due to the LSPR effect of Au clusters. XPS analysis shows that in all Au/TiO_2 samples gold was present in the metallic state. The lowest solid-state photoluminescene (PL) intensity, which also means the lowest recombination rate of charge carriers, was exhibited by the Au-1.0% sample, followed by Au-0.7%, Au-0.4%, and Au-0.1 % solids, respectively. The highest visible-light triggered BPA degradation rate was obtained in the presence of Au-1.0% catalyst, and the lowest one over the Au-0.1% solid. These findings are in very good agreement with the results of solid-state PL measurements. From the results of photocatalytic runs (BPA oxidation and ROS tests), we can conclude that the oxidation pathway of BPA degradation involves superoxide anion and hydroxyl radicals. It was further revealed that the formation of superoxide anion radicals (i.e. priority ROS to oxidize BPA) increases by increasing Au loading and decreasing Au particle size on the TNR support. $OH^{\bullet}$ radicals which were under visible-light illumination of Au/TiO_2 plasmonic catalysts produced exclusively via homolytic cleavage of H_2O_2 (the latter is produced by liquid-phase reactions involving superoxide anion radicals), play a secondary role in the reaction pathway of BPA oxidation; their formation strongly depends on metal-support interactions and is favoured in the presence of Au/TiO_2 solids with larger Au clusters on the TNR surface (i.e. Au-1.0% catalyst).

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Influence of Butanol Isomers on Photocatalytic Hydrogen Production over Pt doped titanate catalyst

H. Šalipur[1], , M. Huš[2], A. Prašnikar[2], J. Dostanić[1], D. Lončarević[1]

[1]*University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia*
[2]*Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia*
[*]*hristina@ihtm.bg.ac.rs*

Keywords: TiO_2, water splitting, photoreforming, density functional theory.

Introduction. In the recent decades photocatalytic water splitting and alcohol photoreforming are frequently used methods for the conversion of sunlight to hydrogen energy due to its sustainability, environmental-safety, effectiveness and simplicity. Titanate based materials are the most studied photocatalysts combining the photo-activity of TiO_2 and good ion-exchange ability of layered titanates. Platinum (Pt) doping is considered as an effective approach for lowering the overpotential for hydrogen production and suppressing electron-hole recombination which results in improved photocatalytic activity. Alcohols are commonly used compounds in photoreforming process as hole scavengers which can lead to very selective, value-added oxidation products such as aldehydes, ketones, carboxylic acids, and esters. Photocatalytic reforming of primary and secondary alcohol includes α-H atom abstraction, followed by the formation of aldehydes or ketones, respectively. In contrast to primary and secondary alcohols, photoreforming of tertiary alcohols in the absence of an α-H leads to a C−C-bond cleavage [1,2]. In our research, prepared Pt doped titanate catalysts were studied for photocatalytic hydrogen production using 1-butanol, 2-butanol and tert-butanol. The theoretical calculations were used to further elucidate photoreforming mechanism of investigated alcohols.

Experimental/methodology. Pt doped titanate catalysts were synthesized via simple alkaline hydrothermal treatment, incipient wetness impregnation method and temperature programmed reduction. The physico-chemical properties of the prepared catalysts were investigated using various characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 physisorption, diffuse reflectance spectroscopy (DRS), temperature programmed desorption (TPD). The activities of the prepared Pt doped titanate catalysts were tested via photocatalytic water splitting/alcohol photoreforming for hydrogen production under simulated solar light irradiation. The theoretical evaluation using density functional theory (DFT) were performed in GPAW[1] with the projector augmented wave method (PAW) as implemented in the plane-wave approach.

Results and discussion. Photocatalytic hydrogen production efficiency of Pt doped titanate catalysts was related to highly active anatase crystal phase, preserved nanotubular structure and high specific surface area. The result showed that photocatalytic activity is strongly influenced by alcohol structure with the following order: 2-butanol > 1-butanol > tert-butanol, with obtained maximal hydrogen production rate of 7.5 mmol g^{-1} h^{-1}, 5.3 mmol g^{-1} h^{-1} and 2 mmol g^{-1} h^{-1}, respectively. Insights from this study showed that hydrogen production performance is a trade-off between adsorption/desorption rate of investigated alcohols and intermediates/products, as well as hole scavenging ability induced by stability of formed alcohol radical. The combination of theoretical calculation and experimental strategy was crucial for understanding the hole charge transport process and enhanced activity for hydrogen production of Pt doped titanate catalysts.

Acknowledgments
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Genotoxicity evaluation on photocatalysts ZnO and silver-decorated ZnO on onion root cells

Nathpapat Tantisuwichwong[1*], Naruemon Boonso[1], Sirikorn Nunthasumreung[2], Suwat Nanan[3]

[1]*Department of Biology, Faculty of Science, Khon Kaen University, Khon Kaen 40002 Thailand*
[2]*International Demonstration School, Mahidol University, Thailand*
[3]*Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002 Thailand*
[*]*Corresponding Author's E-mail address: naptan@kku.ac.th*

Keywords: photocatalyst, ZnO and Ag-ZnO, *Allium* test, chromosomal abnormalities

Introduction. Recently**,** photocatalysis is widely used for degradation of pollutants that are not readily degraded by conventional methods [1]. ZnO and Ag-ZnO were fabricated and then used as effective sunlight-active photocatalysts. The ZnO photocatalyst was very efficient in photodegradation on a wide range of antibiotics [2]. In addition, Ag-ZnO showed enhanced photocatalytic degradation of both antibiotics and reactive azo dyes [3]. Despite its effectiveness as a photocatalyst, some toxicities of ZnO were reported in microorganisms, algae, plants, and animals [4]. Additionally, cytotoxicity of Ag-ZnO was also reported for humans [5] because the chemical stabilities of ZnO [6] and Ag-ZnO [7] are high. Therefore, the potential threats of these photocatlysts need to be emphasized.

Experimental/methodology. The effects of ZnO and Ag-ZnO concentrations on elongation of onion roots and cell division in onion root tips were investigated. Onion bulbs were allowed to germinate on test tubes containing deionized water for 24 hours. Five maximum root lengths in each bulb were recorded. Then, elongating roots of onion bulbs were treated using solutions of ZnO and Ag-ZnO and deionized water as a control treatment. Four concentrations at 0, 50, 100 and 200 ppm of each photocatalyst were investigated. There were 6 bulbs for each treatment and the experiments were conducted under dim light and dark. Five maximum root lengths for each bulb were measured at an interval of 24 hours for 96 hours. Roots were cut after 96 hours and fixed in Carnoy's fixative solution and then preserved in 70% ethanol. Mitotic cell divisions in root tips were examined using light microscope.

Results and discussion. Similar effects of ZnO and Ag-ZnO were observed and the photocatalysts significantly ($p<0.05$) inhibited root growth at 50, 100 and 200 ppm. More reductions of root lengths occurred with increasing concentration of photocatalysts. However, there were significant differences in root growth under the concentrations of 50, 100 and 200 ppm. After 96 hours of ZnO treatments, root lengths in 0, 50, 100 and 200 ppm were 3.91, 1.05, 0.56 and 0.39 cm, respectively. Under the same period, the corresonding concentration of Ag-ZnO resulted in root lengths of 3.91, 0.79, 0.53 and 0.41 cm, respectively. Over a period of 96 hours, small root growth occurred under 50, 100 and 200 ppm of ZnO and Ag-ZnO indicating that the photocatalysts were not lethal for root growth. Over 96 hours at the same concentration, Ag-ZnO appeared to cause more reduction in root growth than ZnO suggesting that Ag-ZnO was more toxic than ZnO. Chromosome aberation, e.g. chromosome bridge, chromosome fragments and sticky chromosome were observed.

Acknowledgments
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The effects of antibiotic aqueous solution ofloxacin (OFL) and photocatalyst 5Ag-ZnO treated OFL on onion roots and cell division

Natthanet Tantisuwichwong[1], Suwat Nanan[2], Nathpapat Tantisuwichwong[3*]

[1]*Khon Kaen Wittayayon School, Khon Kaen 40002 Thailand*
[2]*Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002 Thailand*
[3]*Department of Biology, Faculty of Science, Khon Kaen University, Khon Kaen 40002 Thailand*
[*]*Corresponding Author's E-mail address: naptan@kku.ac.th*

Keywords: ofloxacin, 5Ag-ZnO, photocatalyst, onion, root length and morphology, cell division

Introduction. Substantial amounts of antibiotic consumption of antibiotics [1] were inevitably accompanied by continuous secretion and release of the drugs to environments [2]. Ofloxacin(OFL), a second generation of fluoroquinolone antibiotics, is more effective than previous generation in treating various bacterial infections [3]. Due to the non-biodegradable nature of OFL, an effective degradation of the OFL is required before discharging the drug to the environment. Fabricated 5Ag-ZnO semiconductor is used as a photocatalyst to degrade OFL, producing OFL metabolites (OMs); nevertheless, OMs still need to be comprehensively investigated for their toxicity.

Experimental/methodology. Two experiments were undertaken. In experiment 1, OFL at a concentration of approximately 10 ppm, OMs containing OFL at a concentration of about 0.15 ppm and deionized water (DW) were assessed for their effects on the elongation of onion roots. Thirthy six onion (*Allium cepa*) bulbs with uniform root growth under DW for 24 hours were used in these experiments. Maximum root lengths were determined for these bulbs. Three groups of 12 onion bulbs were assigned to DW, OFL and OMs treatments, respectively. Maximum root lengths were measured at 24, 48 and 72 hours after applying the treatments. All procedures in experiment 1 were used in experiment 2; however, in this case the growth of onion roots was allowed for 24 hours only prior to taking measurement of maximum root growth. All roots in each bulb were cut and fixed in Carnoy's fixative solution and then transferred to 70% ethanol. Preserved root samples were used to examine cell divisions in root meristematic tissues using a light microscope.

Results and discussion. In experiment 1, abnormal root growths occurred under OMs while normal root growths were observed under DW and OFL. There were no significant differences in maximum root length between DW and OFL treatments over 72 hours and maximun root lengths at 72 hours for DW and OFL were 3.35 ± 0.88 and 3.80 ± 1.09 cm, respectively. However, maximum root lengths treated with OMs were significantly lower ($P<0.05$) than those treated with DW or OFL and maximum root length at 72 hours for the treatment was 1.55 ± 0.42 cm. Crochet root were predominantly presented in onion treated with OMs. In experiment 2, the maximum root lengths were not significantly different between DW and OFL treatments and the lengths were 3.37 ± 0.56 and 3.30 ± 0.45 cm. However, maximum root lengths of 1.93 ± 0.41 cm by OM treatment were significantly lower ($P<0.05$) than those by either DW or OFL treatment. Normal cell division occurred in DW and OFL treatments while aberration of cell division was observed in OMs treatment. Two experiments indicate that OFL is not harmful to onion roots. Although OMs is not lethal to onion root growth, the metabolites exhibit some adverse effects.

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Selective Photocatalytic Reduction of CO_2 to CH_4 over Pd-modified TiO_2 Nanocatalyst

Xiao Tian[1, 2], Xin-ying Liu[1, *], Diane Hildebrandt[3], Fa-tang Li[2, *], Xiao-jing Wang[2]

[1] *University of South Africa, Private Bag X6, Florida, 1710, South Africa*
[2] *Hebei University of Science and Technology, Shijiazhuang, 050018, China*
[3] *University of the Witwatersrand, Johannesburg 2050, South Africa*
[*] *liux@unisa.ac.za, lifatang@126.con*

Keywords: CO_2 reduction, CH_4, Photocatalytic, TiO_2

Global warming caused by the greenhouse effect, which seriously threatens the safety of human life. In the process of photocatalytic reduction of CO_2, photocatalysts convert solar energy into chemical energy, and then reduce CO_2 into valuable compounds, such as CO, CH_4, CH_3OH or other hydrocarbons, thus providing an environment-friendly solution that can promote the recycling of CO_2 and the production of sustainable renewable energy.

A well-designed photocatalyst with excellent activity and selectivity is crucial for photocatalytic CO_2 conversion and utilization. TiO_2 is one of the most promising photocatalysts. However, its excessive surface oxidation potential and insufficient surface active sites inhibit its activity and photocatalytic CO_2 reduction selectivity.

In this work, TiO_2 nanoparticles were successfully prepared by sol-gel method, and the separation and migration efficiency of photogenerated carriers was greatly improved by noble metal Pd modification, thereby greatly improving the photocatalytic CO_2 reduction performance and making the selectivity of CO_2 photocatalytic reduction of CH_4 up to 100%.

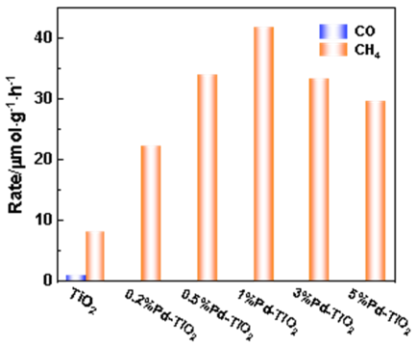

Fig. 1 Comparison of photocatalytic performance of samples

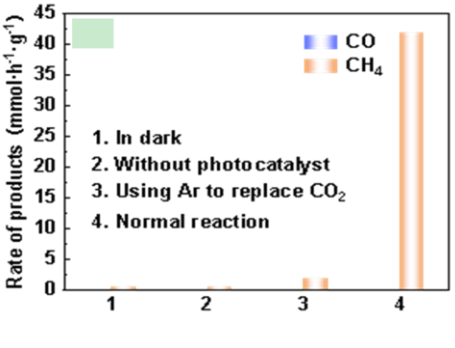

Fig. 2 Photocatalytic performance of 1% Pd-TiO_2 under various conditions

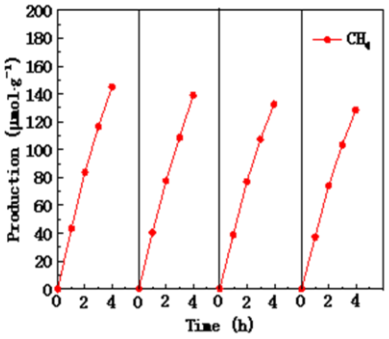

Fig. 3 Cyclic experiment of 1% Pd-TiO_2

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Evaluation of photocatalytic particles deposition techniques to fibrous membranes for pollutant degradation

Z. Vilamova[1*], M. J. Sampaio[2], L. Svoboda[1], J. Bednar[1], Z. Simonova[1], R. Dvorsky[1], C.G. Silva[2] and J. L. Faria[2]

[1] *Nanotechnology Centre, CEET, VSB – Technical University of Ostrava, Czech Republic*
[2] *Laboratory of Separation and Reaction Engineering, Laboratory of Catalysis and Materials, Department of Chemical Engineering, Faculty of Engineering of the University of Porto, Portugal*

[*] *zuzana.vilamova@vsb.cz*

Introduction.

In recent times, fibrous membranes have developed a crucial role in the filtration of pollutants from water [1] or air [2]. Unfortunately, if the filter membrane is used for several hours or days, it leads to a gradually increasing concentration of pollutants on the membrane surface. However, this contamination can be effectively eliminated by the presence of photocatalytic submicroparticles as part of the fibrous membrane. Titanium dioxide and zinc oxide photocatalysts can be found as part of filters for wastewater [2] or air [1] treatment, but their high band gap energy and toxic properties [3] limit their use. However, graphitic carbon nitride (g-C_3N_4) proved its antibacterial properties while maintaining its non-toxic character [4]. It is a semiconducting metal-free photocatalyst, whose easy synthesis, low band gap energy (2.7 eV), easy functionalization, and high physicochemical stability predispose it to be used in the photodegradation of organic pollutants [4] and pathogenic microorganisms [4].

Experimental/methodology.

The Nanospider NS 1WS500U (Elmarco, Czech Republic) equipment was used for membrane preparations. The neat PVB (Mowital 60BHH) solution was stirred over-night at room temperature in an isopropyl alcohol solution to final 8 wt% concentration, than electrospun at 21 °C, 36.5 % humidity; the distance was set at 20 cm; high voltage was set at 55 kV; substrate-shift set at 5 mm/min. PVB_blend was prepared by electrospinning method as well. PVB+g-C_3N_4 (8:1) blend was prepared in an isopropyl alcohol to final 8 wt% PVB concentration. The experiment was performed at same conditions as PVB_neat. The PVB_thermal membrane was prepared as follow: 1 g of g-C_3N_4 was dispersed in aquatic environment (100 ml), then neat membrane (PVB_neat) was added to this solution and heated for 24 hours at 40 ºC in oven and label as PVB_thermal. Last membrane was prepared by combination of blend and thermal methods.

Results and discussion.

Polyvinylbutyral (PVB) fibrous membranes were prepared by the electrospinning method, and their photocatalytic activities were tested by degradation of phenol. The blend method is the most widely used. Active particles are added to the polymer solution prior to the electrospinning process. This approach seems logical and effective. Unfortunately, this method led to particle encapsulation by a polymer within the fiber and to a decrease in photocatalytic activity ($k = 0.00115\ min^{-1}$). Another method is called thermal treatment. This method led to the attachment of the particle to the fiber surface, allowing its significantly more effective surface action ($k = 0.00176\ min^{-1}$). However, the thermal method caused changes in the fiber size distribution. Using a combination of the methods mentioned above, the last membrane was prepared and tested with the highest photocatalytic activity ($k = 0.00281\ min^{-1}$). However, electrons and holes of active g-C_3N_4 caused rapid polymer degradation.

Acknowledgments

This work was supported by the student project SP2023/095 of the VSB-Technical University of Ostrava.

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Photodegradation of sulfamethoxazole by graphene-like biochar doped TiO_2 irradiated with simulated sunlight

C. Yuan*[,1], C.-H. Hung[2], J.-H. Lin[1], Y.-D. Dai[1]

Department of Civil and Environmental Engineering, National University of Kaohsiung, Kaohsiung, Taiwan
Department of Safty, Health, and Environmnrtal Engineering, National Kaohsiung University of Science and Technology

* Ching Yuan, (E-mail:caroline@nuk.edu.tw)

Keywords: Sulfamethoxazole, Graphene-like biochar, Iodine, photodegradation, simulated sunlight

Introduction.

Sulfamethoxazole (SMX) is an antibiotic widely used in the treatment of human and animal diseases. It has been detected in wastewater effluent and aqueous environment. Owing to a long half-life of 85-100 days, a long-term accumulation in the ecosystem causing drug resistance was found [1]. Titanium dioxide is one of the commonly used photocatalysts, which possesses advantages of non-toxicity, low cost, and high photochemical stability. However, its high energy gap makes it impossible to apply to visible light. Doping non-metal elements into TiO_2 is an efficient solution way to shorten the energy gap of photocatalyst. The non-metal elements of N, C, S, I, B, F, and P are often used as doppants. Among which, iodine (I^{5+}) and Ti^{4+} have similar ionic radii to introduce the I5p orbital slightly higher than the valence band of TiO_2, resulting in red-shift of the chracteristics wavelength of photocatalyst [2,3]. The graphene-like biochar prepared from wasted Lanyu podocarp (B) possesses high conductivity to increasing photodegradation, and ecocomical value enhancement for agricultural wastes.

Experimental/methodology.

The B/I-TiO_2 photocatalyst was synthesized by sol-gel and hydrothermal method and SMX was ptotodefraded under simulated sunlight. The surface characteristics of graphene-like biochar, including specific surface area, graphitization, lattice arrangement, surface charge, were characteristized. In this study, the doping amount of iodine and graphene-like biochar, the pH value, free radical identification, and the useful life of B/I-TiO_2 photocatalyst were investigated.

Results and discussion.

It was found that the disordered structure could be transformed into a graphite microcrystalline structure through hydrothermal activation treatment. Prolonging the hydrothermal time helps to shrink the graphite-like d-spacing of graphene biochar and improving the degree of graphitization of graphene-like biochar. At pyrolysis temperature of 700 ℃ and 900 ℃, a long-term hydrothermal activation time of 6 hours will reduce the total pore volume, decreasing the specific surface area from 1036 and 947 m^2/g to 825 and 88 m^2/g, respectively.

The doppants of iodine and graphene-like biochar can effectively shorten the energy gap of TiO_2 from 3.2 to 2.91eV and red-shift the absorbance wavelength to 426 nm, which build a good environmrnt to degrade SMX under a visible light. Moreover, the excited electrons was guided into graphene-like biochar, which good crystallinity could delay the recombination of electron/hole pairs and enhance the efficiency of photodegradation.

Results showed that the removal rate of SMX by 5LB700H2I1T photocatalyst is 40% with a reaction rate constant (k_d) of 1.2×10^{-3} min^{-1}under a pH value of 7, including the adsorption efficiency of 14%, and photodegradation efficiency of 26%. The 5LB700H2I1T is positively charged and could easily attract SMX^- to generate an electrostatic effect, thereby improving the adsorption and photocatalytic degradation performance. The adsorption removal efficiency of SMX is positively correlated with the doping amount of graphene-like biochar. After three-time cycle of photodegradation test, the removal efficiency of SMX only decreased by 2%. A good reusability and high stability of prepared B/I-TiO_2 photocatalysts were verified.

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Influence of Schottky barrier height on the photo/thermal catalytic activity of TiO_2+Pt catalysts

G. Žerjav[1*], A. Pintar[1]

[1]*National Institute of Chemistry, Ljubljana, Slovenia*
[*]*gregor.zerjav@ki.si*

Keywords: plasmonic noble metal, visible-light illumination, Schottky barrier height, photothermal catalysis

Introduction. The plasmonic properties of noble metals (Au, Ag, Pt, etc.) can trigger the photocatalytic activity of the wide band-gap semiconductor TiO_2 under visible-light illumination [1,2]. In this case noble metals, if illuminated with light with wavelength equal or greater than their surface plasmon resonance, generate "hot electrons". The generated "hot electrons" are further injected into the conduction band of TiO_2. The efficiency of the plasmon induced "hot electron" injection is influenced by the height of the Schottky barrier (SB) at the junction between the noble metal and the TiO_2 support [1,2]. The aims of the present study were (i) to investigate in detail how the optical, electronic and catalytic properties of TiO_2+Pt catalysts with 1 wt.% Pt loading depend on the textural and morphological properties of the TiO_2 support, (ii) to use the X-ray photoelectron spectroscopy (XPS) technique to determine the height of SB (SBH), and (iii) to investigate the multifunctional use of the prepared TiO_2+Pt catalysts by using the same material as a photo, thermal and photothermal catalyst in various environmental cleaning applications.

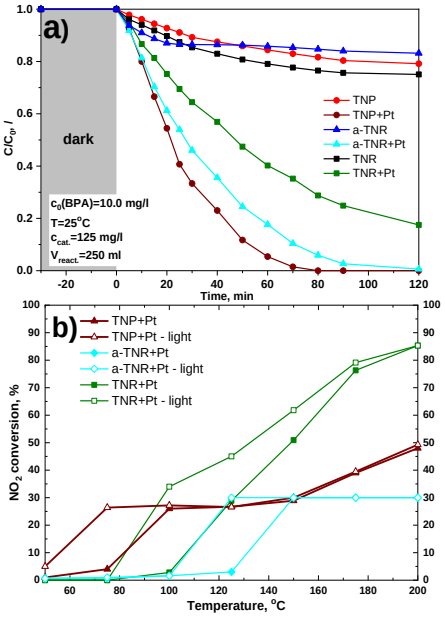

Figure 1. (a) Photocatalytic degradation of aqueous BPA conducted in the presence of investigated catalysts under visible-light illumination. (b) NO_2 conversion vs. temperature curves (solid symbols) and visible-light assisted NO_2 conversion vs. temperature curves (open symbols) over prepared TiO_2+Pt catalysts.

Experimental/methodology. TiO_2+Pt plasmonic solids with 1 wt.% Pt and different TiO_2 supports (anatase nanoparticles (TNP, S_{BET}=86 m^2/g), polycrystalline nanorods (a-TNR, S_{BET}=352 m^2/g) and single-crystal anatase nanorods (TNR, S_{BET}=105 m^2/g)) were synthesized by the wet impregnation technique. The ability of the prepared TiO_2+Pt materials to be used as a photocatalyst for the waste water treatment was tested in a batch slurry reactor under visible-light illumination using water-dissolved bisphenol A (BPA) as a model organic pollutant. In addition, the prepared solids were examined in a catalytic model reaction to evaluate the activity during NO_x reduction in the presence of H_2 as a reducing agent, in order to conceptually demonstrate an alternative approach for low-temperature NO_x abatement that was further enhanced/upgraded by photocatalysis where visible-light illumination was employed.

Results and discussion. Due to different charges of the TiO_2 support surfaces, Pt ensembles with different sizes, crystallinities and degrees of interaction with the TiO_2 supports were formed during the catalyst preparation procedures. The SBH were 0.38 eV for a-TNR+Pt, 0.41 eV for TNP+Pt, and 0.50 eV for TNR+Pt samples, respectively. Low visible-light triggered photocatalytic activity of TNR+Pt catalyst toward oxidation of water-dissolved BPA is attributed to its high SBH and active site degradation due to adsorption of BPA and/or BPA products (Fig. 1a). On the other hand, the highest photothermal catalytic H_2 assisted NO_2 reduction rate was exhibited by the TNR+Pt sample (Fig. 1b) that can be ascribed to a narrow particle size distribution of small Pt ensembles, the absence of the Pt catalyzed reduction of the TNR support at higher temperatures, and lower rate of re-injection of "hot electrons" from the TNR support to Pt ensembles.

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CdS-chitosan nanocomposite for efficient visible light-driven photocatalysis.

Ladpeace Mbonnjwa[1], Sive Nosenga[1], Phindile B. Khoza[1]*
University of KwaZulu Natal, Durban, South Africa
*khozap2@ukzn.ac.za

Introduction: As the global population increases and resource-intensive economic development continues, many countries, particularly South Africa, are failing to meet the accelerating water demand. Heterogeneous photocatalysis appears as an emerging destructive technology among the new oxidation methods or advanced oxidation processes.[1] This technology leads to the mineralization of most of the organic pollutants. In this study, CdS nanoparticles were synthesized using the thermal decomposition method, in which the single molecular precursor was decomposed at high temperatures in the presence of a capping agent (TOPO or HDD) to produce monodispersed nanoparticles.[2] The capped CdS nanoparticles were immobilized onto chitosan microbeads for better recyclability and re-usability.The composite of CdS-chitosan was used as a photocatalyst in the degradation of rhodamine-B in an aqueous system.

Experimental: The physical, morphology, and spectroscopic properties of the synthesized CdS, chitosan and CdS/chitosan composites were characterized using the X-ray diffraction spectroscopy (XRD), Fourier transforms infrared spectroscopy (FTIR), Brunauer-Emmett-Teller method (BET), scanning electron microscopy, energy dispersive X-ray mapping (SEM-EDX-mapping), transmission electron microscopy (TEM) with high resolution-transmission electron microscopy (HR-TEM) and UV–Vis, photoluminescence spectroscopy (PL).

Discussion: The composite showed superior photocatalytic performance, nearly seven times higher than the individual components. The high photocatalytic efficiency of the composites may be attributed to the role played by the significantly improved surface area and the occurrence of high photoinduced charge separation, as revealed by the morphological and opto-spectroscopic characterization of the synthesized composites, and photocatalysis experimental data. Furthermore, the composites exhibited excellent recyclability and stability, making it potential candidates for use in environmental remediation.

Keywords:CdS, chitosan; photocatalytic degradation; enrofloxacin; environmental remediation.

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Photocatalytic degradation of micropollutants using TiO_2 on carbon foam

D. Lokhat[1*], E. Kadwa[1], N. Keswa[1], N. Ntshangase, M. Carsky[1]

[1]*School of Engineering, University of KwaZulu-Natal, Durban, South Africa*
[*]*lokhat@ukzn.ac.za*

Keywords: carbon foam, photocatalyst, micropollutant

Introduction. Photocatalysis has been extensively studied as a relatively simple and effective means of degrading micropollutants in water. It is a technique which requires a light source and a material capable of generating free radicals in the reaction medium. Titanium dioxide (TiO_2), a semiconductor material, is a highly effective photocatalytic material. There have been numerous research studies dedicated to the improvement of photocatalytic activity of TiO_2. Furthermore, as a means of avoiding the problems of separation and recovery of the TiO_2 particles, the immobilization of the active component on a support material has also been intensively studied [1]. Amongst the different substrates proposed, carbon foam is a relatively low cost and robust support structure for the immobilization of TiO_2. It has favourable electron transport characteristics and exhibits superior adsorption capability (particularly important for the low concentration of certain micropollutants) which together results in higher photocatalytic activity [2].

Experimental/methodology. In this study, samples of TiO_2 on carbon foam were produced, and the materials were tested as a photocatalyst for the degradation of an organic dye (rhodamine B, which serves as a model micropollutant) in water. The carbon foam was activated with potassium hydroxide before being loaded with the titanium dioxide precursor and calcined. Four different catalysts were prepared, which included activated and unactivated samples, and samples calcined at different temperatures (400-600 °C). The photocatalytic activity of the catalyst was determined through batch studies using a cylindrical glass reactor equipped with a UV lamp.

Results and discussion. The activated carbon foam support gave a photocatalyst with the highest level of anatase TiO_2, which is more effective than the rutile and brokite phases which were detected in the unactivated carbon foam samples. Then percentage removal of dye (by both degradation and adsorption) was the highest in the activated photocatalyst (18.3%). This compared very well to the percentage removal of unsupported TiO_2 (18.5%). The unactivated photocatalyst performed relatively poor, with only 5-8% removal of dye. The activated TiO_2-carbon catalyst was effective for the degradation of rhodamine B dye.

Acknowledgments
This work is based on upon research supported by the National Research Foundation of South Africa and ESKOM.

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Fabrication of Bioinspired TiO_2-CdS Core-Shell Structure for Long-term Stability Hydrogen Evolution Photocatalyst

Jihyun Lee, Azizar Ghufran Aulia, Jongwook Hong, Beom Jin Kim*

Department of Chemistry, University of Ulsan, Ulsan, 44610, Korea
**kimbj@ulsan.ac.kr*

Keywords: bioinspired, photocatalyst, high stability, type-II, hydrogen evolution reaction

Introduction.

Artificial photosynthesis, the process of converting solar energy into chemical energy, offers a viable solution to address the greenhouse effect and the fossil fuel crisis. In this study, an innovative TiO_2-CdS core-shell structure of nanorods was developed as a photocatalyst to enhance photocatalytic efficiency. A bioinspired approach was employed, wherein CdS nanorods were individually encapsulated with a biologically functionalizable TiO_2 layer using a catalytic peptide inspired Nature. This bioinspired approach and compatible reaction conditions enabled the encapsulated CdS nanorods to maintain their stability and original shapes, distinguishing them from conventional TiO_2/CdS photocatalysts. The in-situ decoration of TiO_2 nanoparticles on the surfaces of the CdS nanorods ensured a close contact between the two components. This close connection between CdS and TiO_2, along with the favorable type II heterojunction, promoted effective separation of charge carriers and preserved robust redox properties.

Experimental/methodology.

To synthesize CdS nanorods $CdCl_2 \cdot 2.5H_2O$ and CH_4N_2S were mixed with ethylenediamine and then introduced into the autoclave for 48 hours. Next, CdS nanorods were dispersed in ethanol, and 11-mercaptoundecanoic acid was added. The solution was sonicated for 30 minutes and then heated for one hour. The mixture was centrifuged, and the resulting precipitate CdS-MUA were rinsed with Tris-HCl Buffer before dissolved in peptide. The mixture was then centrifuged for 5 minutes. The collected CdS NPS were immersed in TiBALDH. The peptide deposition and TiO_2 formation cycle was performed several times to create thicker TiO_2 shells. Finally, the prepared samples were calcined for 3 hours.

Results and discussion.

As a result, a significant enhancement in the photocatalytic hydrogen (H_2) evolution reaction and stability over 20 hours was achieved. The H_2 yield rate of the TiO_2-CdS composite reached 3209 $\mu mol\ g^{-1}\ h^{-1}$, which is 6 and 422 times higher than that of pure CdS and TiO_2, respectively. Additionally, when compared to conventional methods, the photocatalytic activity was four times greater. This research offers a novel perspective on the development of type-II scheme photocatalytic systems with optimal performance characteristics.

Nanoplasmonic Effect of Copper Dendrite Catalyst on Efficient Potoelectrochemical H_2O_2 Detection and SERS Substrate

Yu-Kuei Hsu[1*], Cing-Ren Shih[1]

[1] *Department of Opto-Electronic Engineering, National Dong Hwa University, Hualien, Taiwan*
[*] *Corresponding Author's E-mail address: ykhsu@gms.ndhu.edu.tw*

Keywords: Copper, Electrochemical Detection, Plasmon

Introduction.

The unique plasmonic properties of metallic nanoparticle catalysts have placed them in a privileged spot among other materials in nanoscience. Plasmonic materials developed so far are typically made of gold and silver. The relative high cost of gold and silver hinders the commercialization of plasmonic materials. Hence, it is significant to search for low-cost and earth-abundant materials for plasmonic applications. Copper (Cu) is much less expensive than gold, and its nanostructures have been proposed for a number of applications within photonics, catalysis, nanothermometry, biosensing or nanomedicine. In this study, facile and one pot-synthesis of Cu NDs was fabricated by Galvanic replacement reaction through immersing the aluminum (Al) foil in the copper sulfate solution at room temperature for 1 h. The dendrite-like Cu nanostructure on Al foil was further functioned as SERS substrate and PEC H2O2 sensor without enzyme under the LSPR-mediated effect.

Experimental/methodology.

The schematic growth of Cu NDs on Al foil was fabricated via a Galvanic replacement reaction, as shown in Fig. 1a. Typically, 12.5 mM $CuSO_4$ was dissolved in 25 mM HCl aqueous solution. An Al foil (1×2 cm^2) was washed using diluted hydrochloric acid and then rinsed with distilled water three times. After being dried by flowing nitrogen gas, the Al foil was immersed in the $CuSO_4$ solution. Red copper metallic particles formed on the Al foil in a few minutes with effervescence, and Cu NDs were produced on the surface of Al foil for 1 hour.

Results and discussion.

In order to probe the SERS detection limit of Cu NDs/Al foil substrate, the samples were immersed into the different concentration of 4-MBA solutions. The results show the Raman spectra from the leaf-like Cu nanostructures with 4-MBA concentrations varied from 1×10^{-1} to 1×10^{-7} M. Obviously the signals gradually decrease with decreasing the 4-MBA concentration. We could clearly observe 4-MBA Raman signals when a solution with a concentration as low as 0.1 μM was used. Finally, the EF value was calculated to be about 10^6. The enhancement factor as high as 7×10^6 revealed the 3D Cu NDs on Al foil could be used as effective SERS substrate in trace detection.

To further verify the LSPR-enhanced H2O2 reaction on Cu NDs/Al foil electrode, the effect of excitation intensity and wavelength on the electrocatalytic performance was studied. The results shows that the plasma-enhanced H2O2 reduction current of Cu NDs increases significantly with an illumination intensity of a 450 nm light source and is linearly dependent. Importantly, this linear dependence can rule out the effect of photo-thermal heating and prove to be a characteristic of hot charge carriers related to photochemical reactions, revealing more production of hot charge carriers at a higher illumination intensity. In addition, the excitation wavelength-dependent steady-state currents of H2O2 reduction on the Cu NDs electrode at -0.4 V were measured to probe the LSPR-accelerated effect. The steady state current varies significantly with five separate wavelengths, showing a red-shift trend to the LSPR spectrum of Cu NDs. This shift corresponds to the increase of the refractive index around Cu NDs, in relation with optical changes involving the formation and structuring of complexes. Except for the red-shift, it almost overlaps with the plasma excitation peak of Cu NDs, indicating that LSPR excitation should be the main factor leading to the observed increase in current. Therefore, we attribute the dramatic enhancement in cathodic current of H2O2 electro-reduction to the LSPR effect of the Cu NDs.

Acknowledgments

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Treatment of flue / exhaust gases

Catalyst Adhesion Enhancement Technology for Metallic Honeycomb Substrates for Energy and Environmental Applications Using Special Coating Techniques

J.-H. Choi[1*], G. Kim[1], H. Jeong[1]

[1] *Korea Institute of Materials Science, Changwon, Gyeongnam 51508, Republic of Korea*
[*] *jchoi@kims.re.kr*

Keywords: catalyst adhesion, metallic honeycomb substrate, powder spray coating, intermediate layer

Introduction. Wash-coating methods have been widely used to coat environmental catalysts on ceramic and metallic honeycomb substrates. Adhesion strength of conventional wash-coated catalysts on metallic substrates, however, might not be enough especially for exhaust gas after-treatment applications demanding high mechanical durability. The wash-coated layer of ceramic-based catalysts on the metallic surface tends to be easily detached because bonding property between ceramic and metallic materials is basically not good. Herein, a special ceramic powder spray coating (PSC) method and some other techinques were adopted to greatly enhance the adhesion strength of catalysts on metal honeycomb substrates for energy and environmental applications.

Experimental/methodology. Honeycomb metallic monolith catalysts were prepared using the powder spray coating and conventional wash-coating techniques and their catalyst adhesion strength and performance were compared using an in-house lab bench system. The PSC technique was applied to form oxide-based intermediate layer [1] or to directly coat catalyst powders on the substrates. Some other techniques such as substrate andizing [2] and pack cementation [3] were also used to form the oxide intermediate layers on metallic substrates.

Results and discussion. The powder spray coating technique without using any binding material was successfully applied to form the dense intermediate layer with well-adhered interface and rough surface without pore or crack on metallic honeycomb substrates [1]. Metallic monolith catalysts with the intermediate layer showed much better washcoat adhesion property than those without the intermediate layer even with high washcoat loading. De-NOx conversion efficiency of the metallic monolith catalysts having the intermediate layer was much higher than those without the layer after the ultrasonic vibration test to evaluate the adhesion property [1]. The intermediate layer formation, therefore, could considerably increase the washcoat adhesion strength of metallic monolith catalysts to enhance their long-term mechanical stability. Monolith catalysts having a Fe-ZSM5 layer directly coated on stainless steel sheets using the PSC method also showed super-strong adhesion property and high NOx removal performance comparable to that of wash-coated catalysts for both standard and fast NH_3-SCR reactions.

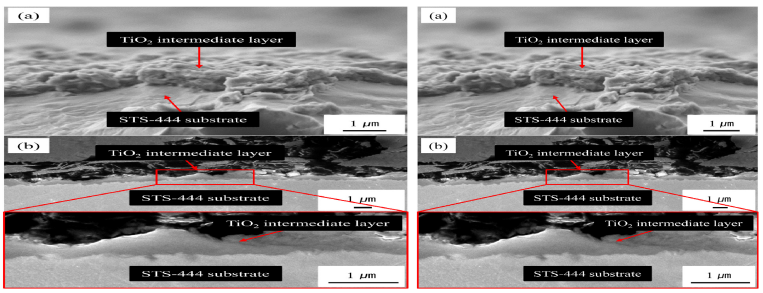

Fig. 1. Intermediate layer formed by PSC

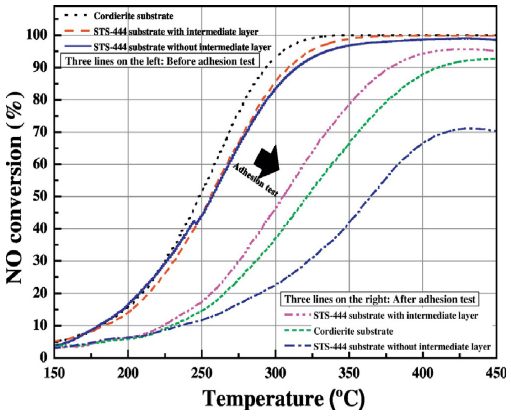

Fig. 2. NO conversion test results

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Synthesis of Palladium-based nanoparticles with tuneable sizes for catalytic applications

Anastasia Kappelou[1*], Nicoleta Muresan[2], David Thompsett[2], Laura Torrente[1]

1. University of Cambridge, Cambridge, United Kingdom.
2. Johnson Matthey Plc, United Kingdom.
[*]Anastasia Kappelou: ak2121@cam.ac.uk

Keywords: nanoparticles, microfluidics, microreactors

Introduction. Metallic palladium and palladium-based nanoparticles have been extensively studied in a wide range of catalytic applications, including their use in air pollution remediation catalysts in the automotive industry[1,2]. However, the relationships between their catalytic activity and size and composition remains unknown due to the dynamic structure of the nanoparticles under catalytic conditions.
This work demonstrates the continuous synthesis of palladium-based nanoparticles with controllable sizes and a narrow size distribution using continuous flow microreactors for catalytic applications. This new method enables for the first time, the elucidation of size-activity relationships, decoupling size and supports effects. In addition, the easy scale-up of the method can lead to a new way of designing and manufacturing catalysts.

Experimental/methodology. Flow microreactors are used for the continuous synthesis of Pd nanoparticles from palladium nitrate precursors and sodium borohydride. The reactants were injected using syringe pumps at a controlled flow rate and both reactants molar concentrations were kept constant. In this study, the 3D configuration of microreactors enables continuous colloidal synthesis of palladium oxide nanoparticles through hydrolysis and palladium nanoparticles through reduction methods. The combination of laminar flow in the microreactors (characterised by low Reynolds numbers) and the promotion of transitional flows (i.e. Langragian turbulence) through 3D configurations leads to a narrow residence times which is translated into narrow size distributions even in the absence of steric capping ligands.[3]

Results and discussion. This study investigates the effect of different palladium precursors on the rate of reaction and stability during the synthesis. Palladium oxide (PdO) nanoparticles of sub 5 nm size and metallic palladium nanoparticles with tunable sizes below 10 nm are synthesised. The results reveal the higher instability of the Pd nanoparticles with respect to PdO counterparts in the absence of capping ligands. In this work, we demonstrate that manipulation of initial precursor speciation can greatly affect the stability of resulting nanoparticles and allowing their synthesis in the absence of in-situ capping ligands and stabilisers.
Tunable sizes of these Pd-based nanoparticles are synthesised and deposited onto ceria supports in order to be used as model catalysts for three-way catalysis. The variation in nanoparticles size of active metal affects the number of uncoordinated sites available for the reactions to occur and the different species of Pd-based nanoparticles present on the surface affect the dynamic behaviour and mechanism of the reaction. The synthesised materials will be tested for their catalytic activity and compared against benchmark catalysts.

Acknowledgments

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Atomically Dispersed High-Performance Metal Ensemble Catalysts for Pollution Remediation beyond Single-Atom Catalysts

H. Jeong[1*], G. Kim[1], J.-H. Choi[1]

[1] *Department of Functional Ceramics, Korea Institute of Materials Science (KIMS), Changwon, Gyeongnam 51508, Republic of Korea*
[*] *hjeong@kims.re.kr*

Keywords: full dispersion, atomic arrangement, ensemble, single-atom, three-way catalysis

Introduction. The single-atom catalysts (SACs), in which all the metal atoms are isolated on the support with 100% dispersion, have received much attention due to unique catalytic performace [1]. However, SACs cannot catalyze propane or propylene oxidation requiring metal ensemble sites to cleave C-C bonds [2]. Thus, atomically dispersed catalysts with ensemble sites are highly desired. In this work, we prepare metal (Pt, Pd, and Rh) ensemble catalysts (ESCs) with 100% dispersion and use them for three-way catalysis.

Experimental/methodology. Commercial γ-alumina was activated by pre-reduction (rAl_2O_3) to create coordinatively unsaturated Al^{3+}_{penta} sites [3]. Ceria species were impregnated to the rAl_2O_3, and then defective ceria nanoparticles were formed on the Al^{3+}_{penta} sites (CeO_2-rAl_2O_3) with many Ce^{3+} sites. Then, metal species (Pt, Pd, and Rh) were impregnated slowly on the defective ceria at 40 °C, resulting in ESCs.

Results and discussion. The ESCs had 100% dispersion as confirmed by CO and H_2 chemisorption. The diffuse reflectance infrared Fourier-transform (DRIFT), extended X-ray absorption fine structure (EXAFS), and high angle-annular dark field scanning transmission electron microscopy (HAADF-STEM) results clearly showed the atomically dispersed metal ensemble structure. When the ESCs and SACs were employed to three-way catalysis, the ESCs showed excellent low-temperature activity for the oxidation of CO, C_3H_6, and C_3H_8 and the reduction of NO (Figure 1). However, the SACs showed poor activity for the simultaneous reaction due to competitive adsorption by unreacted hydrocarbons. The ESCs showed outstanding durability against hydrothermal aging at 900 °C for 24 h, long-term reaction for 420 h, and recycle tests.

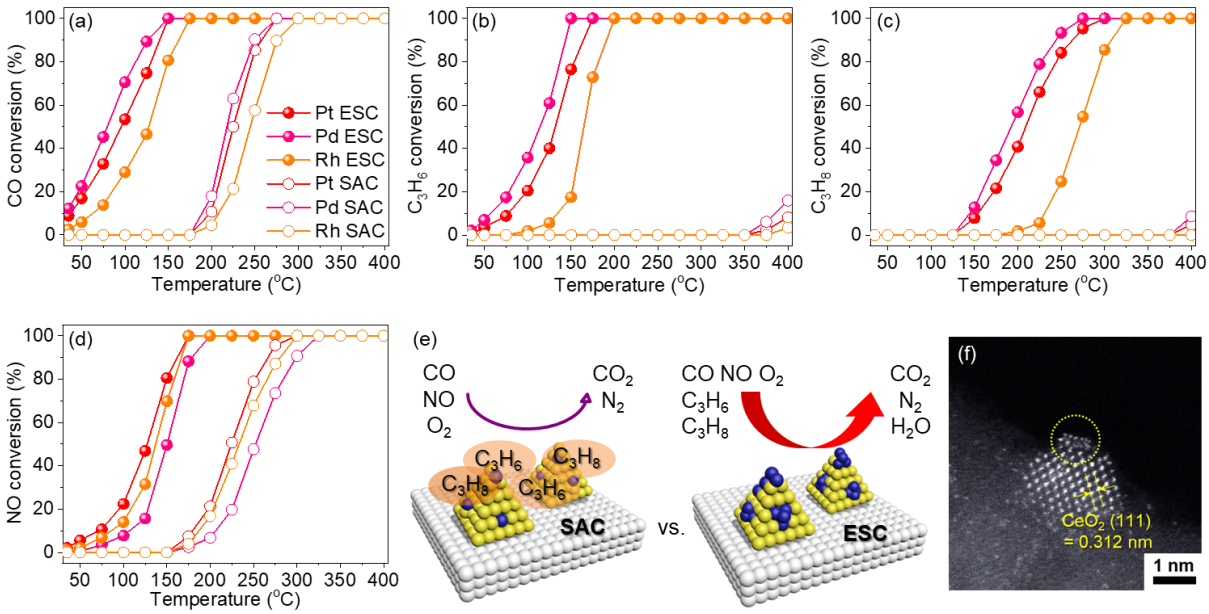

Figure 1. Catalytic performance of ESCs and SACs for a three-way catalysis: (a) CO conversion, (b) C_3H_6 conversion, (c) C_3H_8 conversion, and (d) NO conversion. (e) Schematic comparison of SAC and ESC. (f) STEM image of Pt ESC.

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Enhancing the catalytic activity of Pd-based catalysts for methane oxidation by oxygen oscillations: From understanding catalysis in the laboratory to engine test rig experiments

O. Kröcher[1,2*], M. Roger[1,2], M. Wang[2,3], P. Dimopoulos Eggenschwiler[3], D. Ferri[1]

[1]*Paul Scherrer Insitut, Villigen, Switzerland*
[2]*EPFL, Institute for Chemical Sciences and Engineering, Lausanne, Switzerland*
[3]*EMPA, Dübendorf, Switzerland*
[*]*oliver.kroecher@psi.ch*

Introduction. Methane from biomass and CO_2 is considered as one the most promising fuels for a future sustainable energy system. However, the use of methane as fuel in internal combustion engines is associated with the emission of considerable amounts of unburned methane with a GWP of 27.9 compared to CO_2. Efficient catalysts for methane emission control are mainly based on palladium that suffer from high light-off temperatures that are often above the actual exhaust gas temperatures. We have recently shown that short reducing pulses (SRP) strongly enhance the methane oxidation activity of Pd-based zeolite catalysts [1]. In this study, we have expanded this concept of oxygen oscillations to more practice-relevant Pd-based catalysts and three-way-catalysts (TWC) under both lean and stoichiometric conditions, by combining lab reactor tests, operando spectroscopy and engine test rig experiments.
Experimental/methodology. 2 wt % Pd/Al_2O_3 [2] and $Pd\text{-}Rh/Al_2O_3$ were prepared as model catalysts by wet impregnation, followed by calcination at 500 °C for 2 h. 1.6. wt% Pd/Al_2O_3 doped with La [3], a commercial Pd/Rh TWC [4,5] as well as Pd, Pt-Rh, Pd-Rh and Pt-Pd-Rh on alumina and ceria-zirconia coated on ceramic monoliths were provided by Umicore [6]. Powder as well as monolith catalyst tests were conducted in suitable model gas reactors in the laboratory equipped with fast gas dosage switching and FTIR as well as MS gas analytics. Selected model catalysts were characterized ICP-OES, N_2 physisorption, SEM/EDX, TEM, in situ DRIFTS, XRD, operando XANES and in situ XPS. The large catalyst samples from Umicore were also tested on a heavy-duty 4-cylinder natural gas engine under stoichiometric conditions.
Results and discussion. Under lean operating conditions, methane was oxidized by oxygen in the steady-state. By applying SRP, the activity of Pd/Al_2O_3 was enhanced by activation of the steam refoming (SR) reaction associated with a significant drop in the apparent activation energy. Fit of time-resolved operando XAS data using kinetic models of oxidation revealed that only moderately active PdO existed under static operation, while during SRP operation highly active PdO_x species were formed and maintained by the presence of metallic Pd. A practical range of Pd oxidation degree with 25–65% Pd was found to be optimal to preserve high CH_4 conversion [2]. Under stoichiometric operating conditions, periodic lean-rich switches not only improved methane oxidation but also NO reduction over Pd/Al_2O_3 as model TWC [3]. The effect of O_2 pulses on the methane conversion could be calculated and predicted reliably. The results found in the laboratory over Pd/Al_2O_3 under TWC conditions could be confirmed at the engine test rig with a commercial Pd-Rh catalyst [4]. Whereas direct oxidation was the only CH_4 conversion pathway in steady-state, the high conversion under transient conditions was due to SR. During oscillations a characteristic “W” shape of the methane concentration profile was found that could be explained by different reaction regimes linked to catalyst oxidation and adsorbed surface carbonaceous species [5]. Among the different PGM combinations Pd-Rh proved to be best suited, since it kept SR active for longer time after transition from lean to rich [6].

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Interplay of Pd nanostructure with redox properties of CeO_x and its influence on CO oxidation activity of Pd/CeO_2-TiO_2 catalysts

J. Mosrati[1], H. Atia[1], S. Bartling[1], S. Wohlrab[1], A. Abdel-Mageed[1*]

[1]*Leibniz-Institut für Katalyse, Albert-Einstein-Str. 29A, 18059 Rostock, Germany,*
[*]*ali.abdelmageed@catalysis.de*

Introduction. Supported Pd catalysts are considered amongst the most active in several catalytic processes, in particular for environmental catalytic applications (e.g., methane/CO oxidation, hydro-dehalogenation) [1]. Despite their high activity the use of these catalysts may be limited on the long run by the high price, especially with the expected increase of their demand in several applications [1]. Therefore, development of strategies to rationalize the use of active Pd species and a enhancing their stability under reaction conditions is indispensable. This can be achieved by stabilization of small Pd nanostructures (single atoms, clusters, 2D-rafts) on oxide surfaces. Recently, we showed that sol-gel prepared CeO_2-TiO_2 supports are good candidates for stabilizing highly dispersed Cu atoms with the big advantage of enhancing the Ce3+ /Ce4+ redox shuttle [2]. In this work we employed a structurally optimized CeO_2-TiO_2 supports to prepare Pd/CeO_2-TiO_2 catalysts with different Pd nanostructures achieved by controlled variation of Pd loading and preparation method. Herein, we aim at understanding the interplay of different Pd nanostructures with support redox properties and their influence on the catalytic activity in CO oxidation under a kinetically controlled regime. A multitude of characterization methods, including in-situ/operando spectroscopic techniques have been applied.

Experimental/methodology. Pd/CeO_2-TiO_2 catalysts with different Pd loadings were synthesized using a one-step sol-gel method (details in Ref.[2]) or using wetness impregnation for comparison. Catalytic activity measurements were done in a fixed-bed flow reactor (1% CO, 1% O_2, He balance). Catalysts were characterized using surface/bulk sensitive methods including, N_2 adsorption, X-ray diffraction, temperature programmed reduction (H_2-TPR), near ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS), and X-ray absorption spectroscopy (XANES/EXAFS) at Pd K-edge (SAMBA beamline, Soleil Synchrotrone).

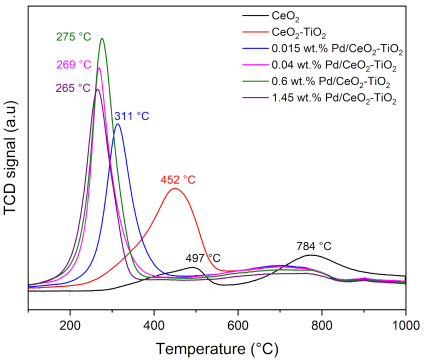

Figure. 1 H_2-TPR profiles of bare support and the Pd supported on CeO_2-TiO_2.

Results and discussion. The Pd mass-normalized activity/turnover frequencies (TOFs) of Pd/CeO_2-TiO_2 with trace amount of Pd (0.1 wt.% - to ensure atomically dispersed Pd according to previous work [2]) display essentially a parabolic dependence of temperature between 80 and 250 °C, with the rate increasing continuously with increasing temperature. Comparison of TOF values at different temperatures for Pd single-atom (Pd-SAC) versus Pd-cluster based catalysts show a complex-structure reactivity pattern and interplay of support reducibility and Pd nanostructure (i.e., Pd-SAC or Pd Cluster). This is represented by tendency for higher activity for Pd-SAC at higher temperatures, and in contrast higher activity for Pd-cluster catalysts at lower temperatures. H_2-TPR showed a shift in CeO_2 surface reduction temperature to lower temperature (**Fig. 1**) on increasing the loading of Pd (i.e., increasing Pd cluster size). In agreement with H_2-TPR, NAP-XPS demonstrated that the presence of Pd on the surface of highly dispersed ceria nanoparticles as small clusters or single atoms promotes the Ce^{4+}/Ce^{3+} redox couple, leading to higher tendency for O-vacancy defects formation[3]. These findings shall be discussed together with detailed XANES/EXAFS results to highlight the complex structure-reactivity relationships of supported Pd catalysts under reaction conditions in an interplay with redox properties of carrying CeO_2-TiO_2 support.

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CO and hydrocarbon oxidation in catalytic particulate filters: Impact of catalyst microstructure and soot deposits

Richard Knopp[1], Miroslav Blažek[1], Aldo Lanza[2], Emily Price[2], Lucy Phillipson[2], Djamela Bounechada[2], Miloš Svoboda[3], Petr Kočí[1*], Andrew York[2]

[1]*University of Chemistry and Technology, Prague, Czech Republic*
[2]*Johnson Matthey Technology Centre, Reading, United Kingdom*
[3]*New Technologies Research Center, University of West Bohemia, Pilsen, Czech Republic*
[*]*petr.koci@vscht.cz, www.vscht.cz/monolith*

Keywords: exhaust gas aftertreatment, reaction kinetics, diffusion, SpaciMS

Introduction

Catalytic particulate filter is a multifunctional device combining catalytic converter with particulate filter. It consists of parallel channels that are alternately plugged at one end [1]. The gas is forced to pass through the porous wall between the channels and the soot particles remain trapped [2]. A catalytically active layer is deposited on and/or inside the filter wall [3]. Its spatial distribution and microstructure influence conversion of gaseous pollutants, pressure drop as well as filtration efficiency [1,2,3].

Experimental

Three catalytic filters were prepared by vacuum deposition of different Pt/γ-Al_2O_3 (0.5% wt.) catalyst slurries on Corning cordierite filter substrate (300 cpsi, wall thickness 200 um, mean pore size 25 µm). The first sample was coated with d_{90} = 0.3 µm catalyst particles forming a thin layer inside wall pores. The second sample was coated with d_{90} = 20 µm slurry that remained mainly on top of the wall. The third sample combined both catalyst locations. All the samples possessed the same total catalyst loading. Tests on all samples included temperature programmed oxidation of CO and octane. The samples were tested as clean, soot-loaded and regenerated. Mercury intrusion porosimetry (MIP), scanning electron microscopy (SEM) and X-ray tomography (XRT) were used to check the structure of catalytic layers. The samples were fouled with 35 nm or 100 nm soot particles and regenerated at 700 °C. Not only the outlet concentrations were measured but also the profiles inside the filter were studied. To do this, two thin capillaries were inserted into the sample, one in the inlet channel and another in in the outlet channel, and the concentration profiles were measured by the SpaciMS technique [4]. The outlet gas composition was analyzed by FTIR MKS 2030 HS and the pressure drop was monitored by a differential pressure sensor.

Results and discussion

The experiments focused on higher gas flow rates that, in addition to catalytic activity, reveal the extent of transport limitations [5]. The measured concentration profiles show that CO and octane slip is distributed uniformly along the entire channel and the samples do not show any non-uniformity of the catalytic layer that would cause a local increase in concentration. The slip is therefore caused by a diffusion limitation at the level of the catalyst microstructure and diminishes at lower flow rates. The samples loaded with soot show somewhat higher slip of unreacted octane, which suggests that soot may act as an additional barrier for reactant diffusion to catalytic centers. The impact of accumulated soot on activity of the individual samples is compared and suitable catalyst microstructures are identified.

Acknowledgments

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Understanding Water-Induced Deactivation of Palladium Based Methane Oxidation Catalysts

S. Mossin[1*], R. L. Mortensen[1,2], K. H. Pedersen, H.-D. Noack, J. Mielby

[1] *Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, Kemitorvet 207, 2800 Kgs. Lyngby, Denmark.*
[2] *Umicore Denmark, Kogle Allé 1, 2970 Hørsholm, Denmark*
[*] *slmo@kemi.dtu.dk*

Keywords: Methane oxidation, Palladium oxide, Catalyst deactivation, Water inhibition

Introduction

Catalysts for complete methane oxidation suffer from water-induced deactivation due to the high concentrations of steam in the exhaust from natural gas-fired large engines. It is commonly accepted that water deactivate the surface through covering the active sites with hydroxyl groups.[1] Here we show through a series of CH_4-TPR and activation measurements that the deactivation takes place by two distinguishable pathways. A reversible deactivation due to surface coverage (inhibition) and an irreversible deactivation due to a structural change in the palladium oxide.

Experimental/methodology.

Palladium oxide (3 wt% Pd) on a modified alumina support was tested in a dedicated catalytic setup fitted with water injection (0-20 vol% water) and methane detector (FID) and with temperature and pressure control (up to 5 bar) during methane oxidation. The catalyst can be repeatedly regenerated to 100% of the original activity using reduction pulses of 1000 ppm methane in nitrogen.[2] CH_4-TPR data was obtained using the same setup as for catalyst testing.

Results and discussion.

Figure 1: Methane oxidation (1000 ppm CH_4, 10 % O_2, 5 % H_2O) of a palladium on alumina catalysts showing the two distinct types of deactivation.

The deactivation profile for both types of deactivation was investigated under a series of different reaction conditions: Temperature, methane concentration, water content, pressure. It is shown that the irreversible deactivation is only taking place when the catalyst is converting methane. The CH_4-TPR performed with and without water reveals a significant shift of the reduction temperature of palladium oxide after the irreversible deactivation.

We show how the rate of deactivation of the catalyst depend on both the water and methane concentration with comparable reaction orders.

On the basis of the results a deactivation model is proposed and we present spectroscopic evidence to suggest the identity of the structural transition taking place during the irreversible deactivation.

Acknowledgments

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Stability of highly dispersed Pd/CeO_2 and Pt/CeO_2 catalysts under realistic three-way catalysis conditions

V. Jestl[1*], V. Muravev[1], T. Bell[2], A. Kolpin[2], D. Thompsett[2], E. Hensen[1]

[1]*Eindhoven University of Technology, Eindhoven, The Netherlands*
[2]*Johnson Matthey Technology Centre, Sonning Common, United Kingdom*
[*]*v.a.j.jestl@tue.nl*

Keywords: three-way catalysis, palladium, platinum, ceria

Introduction. In the field of automotive exhaust treatment and three-way catalysis continuous innovation is needed to meet the increasingly stringent legislative standards that aim to limit emissions from cars with internal combustion engines. Since modern three-way catalysts already operate efficiently at elevated operating temperatures, the focus of current research has shifted towards improving the low-temperature activity of such catalysts and thereby decreasing emissions during the cold start phase of the engine. (1) This is especially important in hybrid vehicles, where the catalyst cools down while driving on battery power. Promising catalysts for low-temperature exhaust aftertreatment are Pd/CeO_2 and Pt/CeO_2 catalysts in which the active metal is highly, possibly atomically dispersed. (2) One of the main reasons why these highly dispersed catalysts are not yet commercially used in three-way catalysis is their limited stability at the high peak temperatures (>1000°C) that can be reached inside a catalytic converter.

Experimental/methodology. In this work, flame-spray pyrolysis (FSP) is used to synthesize ceria nanoparticles containing highly dispersed Pd and Pt. FSP allows for a high degree of control over the ceria particle size in the range of 5 nm to 15 nm with good reproducibility and scalability (Figure 1a). These FSP-made Pd/CeO_2 and Pt/CeO_2 catalysts are then subjected to high temperature hydrothermal conditions as well as realistic aging conditions in a simulated exhaust gas with periodic switches between oxidizing (lean) and reducing (rich) atmospheres. As-synthesized and treated samples are compared in terms of their metal and ceria particle sizes, oxidation states, reducibility and catalytic performance.

Results and discussion. Even though there is significant sintering of the ceria support, hydrothermal treatment has little impact on the metal oxidation state or dispersion of the metal, as evidenced by EXAFS and XPS measurements. Still, hydrothermally treated samples show a lower catalytic activity in CO oxida-tion. In catalysts aged under realistic conditions, significant sintering of Pd and Pt and the emergence of a metallic phase is observed (Figure 1d). A combined XANES/XRD operando study on Pd/CeO_2 showed that such metallic Pd particles form already at 500°C in the CO oxidation reaction under rich conditions, but redisperse under lean conditions (Figures 1b and 1c). These results highlight the significant and complex changes occurring during catalyst aging and show the importance of testing aged materials in addition to fresh catalysts.

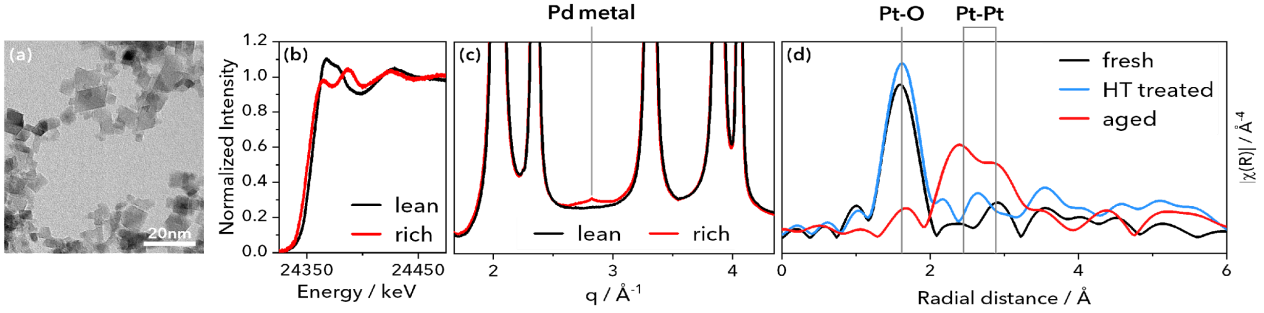

Figure 1 – (a) TEM image of an as-synthesized Pd/CeO_2 catalyst. Formation of metallic Pd particles during CO oxidation under rich (excess CO) conditions at 500°C as evidenced by (b) operando Pd K-edge XANES and (c) operando XRD. (d) Ex situ EXAFS of fresh, hydrothermally (HT) treated and aged Pt/CeO_2 catalysts.

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Intra-catalyst CH_4-oxidation pathways of three-way catalysts and implications on NO_x-conversion profiles for a natural gas vehicle exhaust under lambda modulation

William Partridge[1*], Dhruba J. Deka[1], Calvin Thomas[1], Josh Pihl[1]

[1] *Oak Ridge National Laboratory, 2360 Cherahala Blvd., Knoxville, TN 37932 (United States)*
[*] *partridgewp@ornl.gov*

Introduction. Natural gas (NG) is an attractive alternative to other fossil fuels for internal-combustion engines [1]. NG engines produce little soot and have lower NO_x and CO_2 emissions than diesel engines. Stoichiometric NG engines operate under varying air-to-fuel ratio or lambda (λ) modulation (also known as lean-rich cycling) which creates dynamic exhaust-gas conditions. Three-way catalysts (TWC) are used to control NG engine emissions such as CH_4, CO and NO_x, and their performance can change depending on the modulation-induced compositional changes of the exhaust gas. Understanding how the CH_4 conversion pathways vary along the catalyst and through the λ cycle, how it effects NO_x conversion, and the impact of catlyst formulation is relevant to formulating NG-vehicles after-treatment strategies[2].

Experimental/methodology. Monolith TWC samples with two different oxygen storage materials were used: reference Pd/Al_2O_3-$CeZrO_x$ and PGM-$Mn_{0.5}Fe_{2.5}O_4$. Intra-catalyst Fast-SpaciMS [2] resolved reaction transients along the catalyst flow channel. Lambda-modulation was achieved by dithering the O_2 concentration between Lean (high-O_2) and Rich (low-O_2) at various λ centers, frequencies, and amplitudes. The TWC was operated at 350°C-500°C and with a feed stream containing 0.42% CH_4, 0.45% CO, 0.15% H_2, 0.10% NO, 9.5% CO_2, 18.5% H_2O and varying O_2 flowing at 40,000/h space velocity.

Results and discussion. We performed O_2, CH_4, H_2 and NO measurements at various intra-catalyst locations across a wide range of λ-modulation parameters, and Fig. 1a-b shows the O_2 and CH_4 profiles at a representative condition (amplitude 0.10, λ-center 1, frequency 0.25Hz, temperature 500°C). In the Rich phase, CH_4 steam reforming (SRM) and partial oxidation (POM) area rapidly activated, OSC is consumed, and Pd sites are reduced. In the Lean phase, SRM and POM turn off as the catalyst is reoxidized. Maximum CH_4 conversion occurs around the Rich-Lean transition. At late-Rich times (2s, Fig.1(c) intra-catalyst spatial profile), H_2 is produced from SMR and POM. The NO_x conversion follows CH_4 conversion indicating its dependance on SMR and POM products. At late-Lean times (Fig.1d) SRM, POM and NO_x conversion are only active in the catalyst back. The extent of total oxidation, SRM and POM differed for the spinel catalyst. The dominant CH_4 conversion routes involved SRM and POM for the reference TWC, but surface metallic PGM or oxygen vacancies the spinel-TWC. For both catalysts, λ modulation creates a back-to-front and front-to-back progression of these reactions and catalyst oxidation states through the Rich-Lean λ cycle. This study shows previously unknown dynamic reactions and catalyst oxidation-state waves. Understanding the impact of λ modulation on catalyst performance and the various reaction-zone dynamics will enable control strategies to co-optimize engine efficiency and emissions.

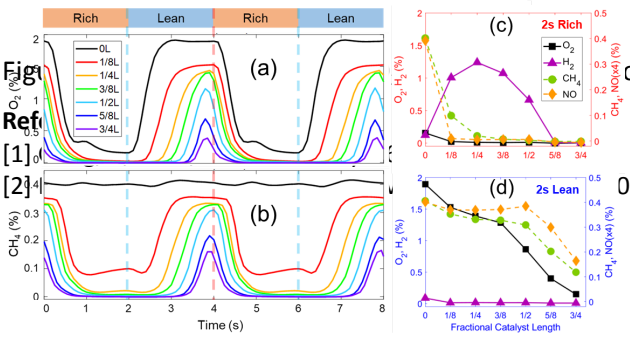

Fig. ofiles: (c) 2s Rich (R-L), (d) 2s Lean (L-R)

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Competition between NO Reduction and NH_3 Oxidation during SCR Reaction on CuSSZ-13 Catalysts Shown by Isotopic $^{15}NH_3$ and $^{18}O_2$ and 2D COS IR Investigations Supported by DFT Modelling

F. Zasada[1], M. Fedyna[1], B.Mozgawa[1], J. Gryboś[1], Ch. Yin[2],
K. Gora-Marek[1], P. Pietrzyk[1], Zhen Zhao[2], Z. Sojka[1]

[1]*Faculty of Chemistry, Jagiellonian University, ul. Gronostajowa 2, 30-387 Krakow, Poland*

[2]*Institute of Catalysis for Energy and Environment, Shenyang Normal University, 110034 Shenyang, China*

[*]*sojka@chemia.uj.edu.pl*

Keywords: NH_3-SCR, Cu-SSZ-13, Reaction Mechanism

Introduction.
Zeolites containing Cu or Fe exhibit high catalytic activity in NH_3-SCR, which is essentially controlled by the nature and nuclearity of the metallic active centers. A comprehansive insight into the SCR reaction mechanism can be obtained from synergy between catalytic studies combined and spectroscopic analysis of the reaction intermediates when isotopically enriched reactants are used, and interpretation of the results is ascertained by DFT modelling combined with ab initio thermodynamic simulations.

Experimental/methodology.
Two types of catalysts of various copper speciation, obtained by impregnation of CHA zeolite with $CuCl_2$ (i-CuSSZ-13) and via one pot synthesis (o-CuSSZ-13), and characterized by SEM/TEM/EDX, MAS-NMR, IR, EPR, and NH3-TPD techniques, were selected as model systems. Their isotopic studies were performaed in TPSR and sready state mode.

Results and discussion.

The isotopic in $O_2/^{15}NH_3$-SCR, $^{18}O_2/NH_3$-SCR and $^{18}O_2/^{15}NH_3$-SCR profiles provided direct evidence that at T < 200 °C the standard SCR reaction occurs alone, whereas at T > 200 °C it is accompanied by ubiquitous intrazoelite oxidation of NH_3 (i-AMO), which involves Cu^{2+}–O^{2-}–Cu^{2+} and Cu^{2+} centers**.** The i-AMO reaction is triggered by temporal excess of NH_3 with respect to NO, caused by release of ammonia stored in the zeolite cages with the increasing temperature. For the i-CuSSZ-13 sample, $^{16}O^{18}O$ production was related to the presence of segregated CuO clusters, revealing that the dissociation of O_2 above 400 °C with formation of peroxy species trigger external NH_3 oxidation (e-AMO). The COS 2D and rapid scan IR and EPR studies along with the constructed 2D thermodynamic diagrams derived from the DFT/FPT modelling alllowed for distinguishing three temperature regions of the SCR/AMO reactions, corresponding to NH_3-reach, lean and dry conditions. and the main processes of each stage were identified. For conceptualization of the SCR reaction, a 2D diagram of stoichiometry, oxidation state and charge compatibility, where the NO and NH_3 reactants and the kye SCR/AMO intermediates are ordered as a function of their oxidation state and the O/H(N) ratio was constructed. The diagram reveals the principal stoichiometry, charge and oxidation state requirements between the reactants and intermediates, and principal modes of their regulation (via OH^- reductive elimination, and H^+/e^- or H^+ transfer), for straightforward turnover of the SCR/AMO reactions. The observed in situ oxidation of excessive NH_3 (i-AMO) in the region of high conversion suggests benefits for the main SCR process from the dynamic adjustment of the ammonia dose at low temperatures, rather than continuously supplying NH_3 at a constant level. This should not only limit the ammonia slip, but also reduce its waste due to considerable unproductive, yet pervasive, oxidation (i-AMO).

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Understanding the influence of Cu-sites during NH_3-SCR of NO_x in the presence of HCHO

Simon Barth[1,2], Deniz Zengel[2], Maria Casapu[2], Jan-Dierk Grunwaldt[1,2*]

[1]*Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, 76344, Germany*
[2]*Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, 76131, Germany*
[*]*grunwaldt@kit.edu*

Introduction.
Oxygenates as renewable fuels generated by conversion of atmospheric CO_2 with renewable hydrogen are promising candidates for achieving carbon neutrality. Furthermore, their combustion leads to the same efficiency as obtained with state-of-the-art diesel engines while less soot formation is observed. Nevertheless, a catalytic after-treatment system is still required, including a NO_x removal catalyst. Due to the incomplete combustion of alternative fuels such as biomethane and oxymethylene ethers (OME), emissions of several hazardous compounds are expected. Herein, formaldehyde (HCHO) is a problematic pollutant since its complete suppression over a standard oxidation catalyst is hardly possible due to external diffusion limitations [1]. Hence, uncovering the influence of HCHO on the NH_3-SCR activity of the NO_x removal system is highly important. In addition, it gives a new insight into the copper species involved.

Experimental/methodology.
A series of Cu-SSZ-13 catalysts with different Cu:Si:Al ratios were prepared similarly as in our earlier work [2, 3]. The resulting powders were coated on cordierite monolith cores (400 cpsi) by dip-coating. Catalytic tests were performed in a stainless-steel reactor from 150-550 °C using a model gas mixture of 0350 ppm NO, 0-350 ppm NH_3, 0-80 ppm HCHO, 10 % O_2, 12 % H_2O in N_2 at a gas hourly space velocity of 100,000 h^{-1}. The gas composition was monitored by a MKS FTIR instrument. Additionally, detailed *ex situ* and *in situ/operando* characterization was conducted to elucidate the relations between catalyst structure, measured activity and byproduct formation.

Results and discussion.
When studying the impact of formaldehyde on the NO_x conversion activity of Cu-SSZ-13, a major drop in the low temperature SCR activity was observed [4]. Furthermore, the conversion of formaldehyde leads to different products depending on the catalyst composition, including the formation of highly toxic HCN emissions. Though, careful tuning of the Cu:Si:Al ratio shows the potential to significantly decrease the HCN emissions. Spatially resolved *operando* XAS measurements performed at the Cu K edge during NO_x removal uncovered a clear impact of formaldehyde presence on the Cu^{2+}/Cu^{+} redox behavior. The obtained results reveal crucial and new mechanistic insights involved in HCN formation as a function of gas mixture, temperature and catalyst composition and at the same time give additional insights into the NH_3-SCR mechanism itself.

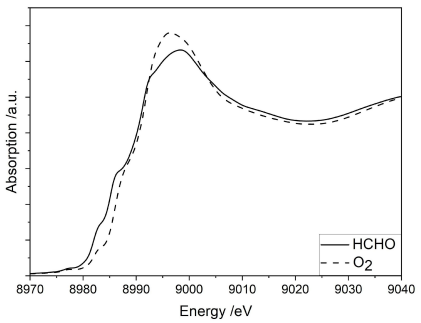

Figure 1: XANES spectra of Cu-SSZ-13 in the presence of HCHO (solid line) and in air (dashed line).

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Sulfur Poisoning of Cu/SSZ-13 Selective Catalytic Reduction Catalysts

W. Epling [1*], Y. Chen[1], P. Rani[1], L. Wei[1], K. Mandal[1], R. Daya[2], C. Paolucci[1]

[1]*University of Virginia, Charlottesville, VA USA*
[2]*Cummins Inc, Columbus, IN USA*
wsepling@virginia.edu

Keywords: emissions control, environmental catalysis

Introduction. Cu-SSZ-13 is widely used as a NO_x reduction catalyst in diesel engine after-treatment systems. However, sulfur, a common component in diesel fuel and oil, can lead to catalyst deactivation. Literature has shown that the relative amounts of Cu sites identified as Z2Cu and ZCuOH lead to different S poisoning extents (1-3) and those relative Cu site amounts can be influenced by mild hydrothermal aging (4,5). Based on these findings, one approach proposed to protect a Cu-SSZ-13 catalyst from sulfur poisoning is to decrease the amount of ZCuOH in favor of more Z2Cu sites, via mild hydrothermal aging.

Experimental/methodology. The Cu-SSZ-13 catalyst was provided by Cummins Inc. and came as a honeycomb monolith structure with a cell density of 300 cells/in^2 (cpsi). Selective catalytic reduction (SCR) experiments were conducted before and after mild hydrothermal aging and sulfur exposure. The samples were also characterized using NH_3 temperature programmed desorption (TPD) and oxidation (TPO), CO, NO and SO_2 oxidation, CO titration, NO + NH_3 titration and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

Results and discussion. SCR of NO_x by NH_3 over the Cu-SSZ-13 sample used can be inhibited by sulfur poisoning. In terms of the commonly identified Cu species in this formulation, literature (1-3) and our own data suggest that a sample with more Z2Cu relative to ZCuOH is less susceptible to sulfur poisoning under some conditions. Furthermore, the catalyst with more ZCuOH appears to be, in general, a better oxidation catalyst. Mild hydrothermal aging induces the migration of the Cu from ZCuOH to Z2Cu and at the same time leads to decreased CO, NO, NH_3 and SO_2 oxidation conversions. DRIFTS also correlates the change in NH_3 oxidation to a change in relative ZCuOH amounts. Our results describe a correlation between the extent of sulfur poisoning to the catalyst's oxidation ability. The results after different sulfur treatments, such as SO_3 exposure, and higher temperature and higher O_2 concentration during SO_2 exposure, all suggest a mechanism where surface SO_2 oxidation leads to more deactivation. This therefore implies that the extent of poisoning is dependent on the oxidation activity of the different Cu species, not solely on their relative amounts.

The above results demonstrate that surface oxidation of SO_2, or the presence of SO_3, leads to more significant catalytic SCR deactivation. And as mentioned above, literature suggests that different Cu species are more or less prone to S poisoning (1-3). We used density functional theory (DFT) and probe reaction experiments to characterize Cu amounts and types, with emphasis on ion-exchanged Cu and multinuclear Cu species. Our results show that multinuclear Cu species are particularly prone to S poisoning, and that the extents of regeneration after exposure are also dependent on S exposure conditions. Overall, the talk will focus on how Cu speciation influences the extent of S poisoning, and which species are more prone to forming stable S-bound species.

Acknowledgments
The authors gratefully acknowledge Cummins Inc for financial support.

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In situ SO_2 poisoning and deactivation measurements of Cu exchanged zeolite catalysts in NH_3-SCR reaction

R. K. Abasabadi[1,2], P. N. R. Vennestrøm[2], F. Wen[3], S. Bordiga[1], E. Borfecchia[1], G. Berlier[1], T. V. W. Janssens[2*]

[1]*Department of Chemistry and NIS Centre, University of Turin, Via Giuria 7, 10125 Turin, Italy*

[2]*Umicore Denmark ApS, Kogle Allé 1, 2970 Hørsholm, Denmark*

[3]*Umicore AG & Co, Rodenbacher Chaussee 4, 63457 Hanau, Germany*

**corresponding author: tonv.w.janssens@eu.umicore.com*

Introduction. Cu exchanged chabazite (CHA) catalysts are applied for selective catalytic reduction of NOx by ammonia (NH_3-SCR) in diesel exhausts. A limitation for application of Cu-CHA is its sensitivity to SO_2 [1]. SO_2 reacts predominantly with $[Cu_2^{II}(NH_3)_4O_2]^{2+}$ complexes, formed upon activation of O_2 in the NH_3-SCR reaction cycle [2,3]. The reaction of SO_2 with $[Cu_2^{II}(NH_3)_4O_2]^{2+}$ leads to reduction of some Cu^{II} to Cu^{I}, in the absence of O_2 [3]. In this work, we show that the uptake of SO_2 is enhanced when O_2 and H_2O are present, and leads to a stronger deactivation of the Cu-CHA catalysts.

Experimental. All measurements were done in a quartz U-tube reactor, connected to a FTIR spectrometer for analysis of the gas composition at the reactor outlet. A series of Cu-CHA catalyst samples (Si/Al ratio 6.7; 3.2 wt% Cu, 10 mg sample size) was pretreated with different methods to form framework bound Cu^{I} and Cu^{II}, mobile $[Cu^{I}(NH_3)_2]^{+}$ and the $[Cu_2^{II}(NH_3)_4O_2]^{2+}$ complex. After the pretreatment, the catalyst was exposed to 100 ppm SO_2, or dry 100 ppm SO_2/10% O_2, or 100 ppm SO_2/10% O_2/5% H_2O mixtures at 200°C for 45 min. The S/Cu ratios were calculated from the measured SO_2 uptakes. To evaluate the deactivation, we express the rate constants for NH_3-SCR at 200 °C after SO_2 exposure as a percentage of the rate constants for the fresh catalysts. For the $[Cu_2^{II}(NH_3)_4O_2]^{2+}$ complex, the SO_2 exposure and activity measurement cycle was repeated 6 times, to achieve a high deactivation and follow deactivation rates.

Results and discussion. Figure 1a shows the deactivation with the S/Cu ratios after the first cycle (black points) for different Cu species in absence and presence of O_2 and H_2O. In absence of O_2 and H_2O, the SO_2 uptake for the $[Cu_2^{II}(NH_3)_4O_2]^{2+}$ complex (star point) is higher, compared to the other Cu species species (green dash circle), in agreement with earlier XAQ and SO_2-TPD results [3]. Addition of O_2 and H_2O leads to a higher uptake of SO_2 up to a S/Cu ratio of about 0.6. The deactivation follows the same trend. The loss of activity is about 1.5-2 times the S/Cu ratio, indicating that a smaller amount of sulfur in the catalyst results in a strong deactivation. This effect is even stronger in the repeated cycles with the $[Cu_2^{II}(NH_3)_4O_2]^{2+}$ complex, where a small S/Cu ratio of 0.3 results in a 82% reduction of the activity. (Red dash line in Figure 1a). This does not follow the same trend as adding O_2 and H_2O, indicating that the S/Cu ratio alone is not sufficient to characterize the deactivation. Figure 1-b shows the deactivation and SO_2 uptake with repeated SO_2 exposure with and without O_2 and H_2O. The presence of O_2 and H_2O accelerates the SO_2 uptake and enhances the deactivation, but in all cases the S/Cu ratio saturates, and some residual activity remains.

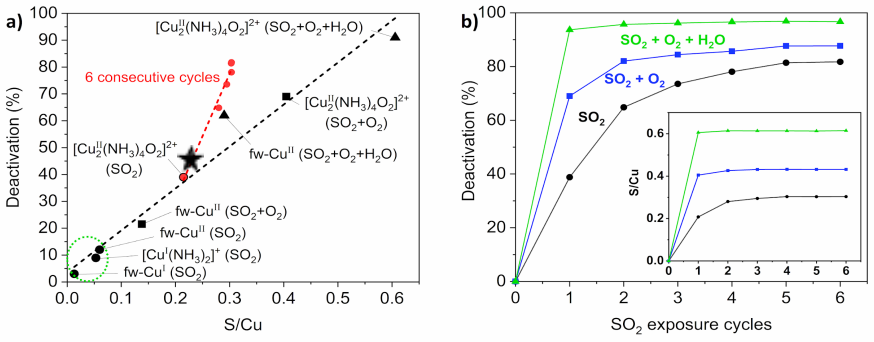

Figure 1- a) Deactivation meaurements versus S/Cu ratios for different Cu species and conditions at 200 °C, b) Measured deactivation and SO_2 uptake (S/Cu ratio) in repeated SO_2 exposure cycles at 200 °C.

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Low-temperature NOx removal (NH_3-SCR) in the presence of water over Sodium Vanadium Bronzes

Yusuke Inomata[1], Hiroe Kubota[2], Yoshinori Honmatsu[3], Sosuke Sakotani[3], Kazuhiro Yoshida[3], Takashi Toyao[2], Ken-ichi Shimizu[2], Toru Murayama[4,*]

[1] *Kumamoto University, Kumamoto, Japan*
[2]*Institute for Catalysis, Hokkaido University, Sapporo, Hokkaido, Japan*
[3]*Energia Economic and Technical Research Institute, the Chugoku Electric Power Company, Incorporated, Higashi-Hiroshima, Hiroshima, Japan*
[4]*Tokyo Metropolitan University, Hachioji, Tokyo, Japan*
[*]*murayama@tmu.ac.jp*

Keywords: NH_3-SCR, NOx removal, vanadium oxide, vanadium bronzes

Introduction. Emission control of NOx (NO and NO_2) is an important task for an industrial chemical process that relies on thermal energy produced by the combustion of fossil fuels. For stationary deNOx systems such as those in coal-fired power plants and waste treatment plants, selective catalytic reduction (SCR) has been used with ammonia as a reducing reagent to convert harmful NOx to harmless N_2 and H_2O [1]. Although the stationary deNOx systems have been successfully established, a conventional catalyst needs a high temperature (>300°C) for NH_3-SCR to proceed. DeNOx catalysts can be moved to the latter part of the system to avoid deactivation if the deNOx catalyst works at a low temperature (~150°C) since the downstream gas is usually cooled down to 100-150°C. We have reported a bulk V_2O_5 and W substituted V_2O_5 catalyst for low-temperature NH_3-SCR (<150°C) under a wet atmosphere [1-3]. In this study, we report a new catalyst for low-temperature de-NOx catalyst based on topotactic material $Na-V_2O_5$.

Experimental/methodology. To obtain $Na-V_2O_5$, NH_4VO_3, $NaNO_3$ and oxalic acid were dissolved in water, and then the solution was heated overnight to evaporate the water on a hotplate. Finally, the resulting solid was calcined at 300°C for 4 h.

Results and discussion. The structure of $Na-V_2O_5$ obtained from the XRD pattern is shown in Fig 1, and the structure of $Na-V_2O_5$ differs from orthorhombic V_2O_5 and $W-V_2O_5$ (Fig. 1a) in that it has a monoclinic crystal structure (Fig. 1b). The reaction rate was calculated at 150°C (Fig. 1c). $Na-V_2O_5$ was more active than the previously reported $W-V_2O_5$, V_2O_5, and $V/W-TiO_2$, which simulates industrial catalysts, and maintained high activity in the presence of 10% water. In the presentation, we will discuss the activity caused by the catalyst structure.

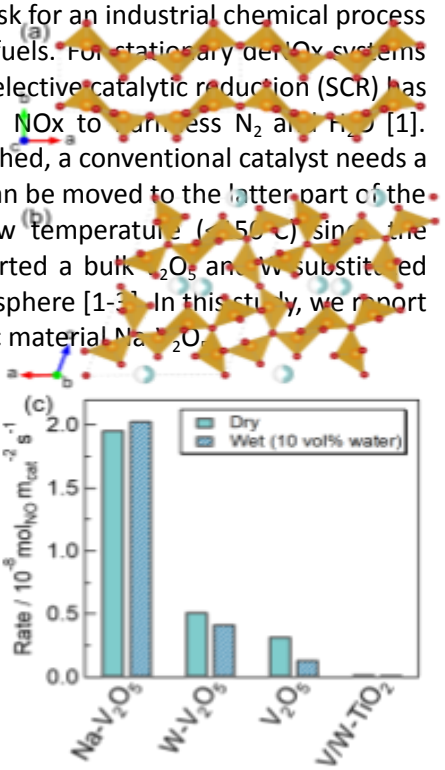

Fig. 1 Structure model of V_2O_5, $W-V_2O_5$ (a), and $Na-V_2O_5$ (b), and the comparison of reaction rate in NH_3-SCR at 150°C.

Acknowledgments

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Coupling RHC and OHC kinetics to close the low-temperature NH_3-SCR redox cycle over Cu-CHA catalysts

N.D. Nasello[1], N. Usberti[1], U. Iacobone[1], F. Gramigni[1], W. Hu[2], S. Liu[2], I. Nova[1], X. Gao[2], E. Tronconi[1*]

[1] *Laboratory of Catalysis and Catalytic Processes, Politecnico di Milano, Milano (Italy)*

[2] *State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou (China)*

**enrico.tronconi@polimi.it*

Keywords: Cu-zeolite, NH_3-SCR, Cu redox, Cu reduction, Cu oxidation, transient kinetic analysis

Introduction.

NH_3-SCR on Cu-zeolite (CHA) catalysts is considered the best available technology to control nitrogen oxides (NOx) emissions from vehicles [1,2]. Recently, great attention has been paid to the low-temperature (LT, ≤250°C) reaction mechanism. Cu sites are involved in a redox process, cycling between Cu^{2+} to Cu^{+} in the reduction (RHC) and Cu^{+} to Cu^{2+} in the oxidation (OHC) half-cycles. Nevertheless, a fully consistent kinetic description of the catalytic redox scheme is still debated [1-4]. Herein, RHC and OHC kinetics are independently assessed and then combined to predict the closure of the LT STD-SCR redox mechanism.

Experimental/methodology.

Tests were run over a model Cu-CHA catalyst (powders, 32 mg, Cu loading =1.8% w/w, SAR =25) at low temperature (150-200°C) in the presence of 2% v/v H_2O. Three main protocols were executed: i) isothermal oxidation of a fully reduced catalyst with O_2; ii) isothermal reduction of a fully oxidized catalyst with NO=NH_3=500 ppm; iii) O_2 feed step changes going from Standard-SCR (STD, NO+NH_3+O_2) to pure reduction (NO+NH_3) conditions, and vice versa. The experimental data were fitted according to a transient integral PFR model of the test reactor (cascade of 20 CSTRs) assuming: a) the RHC rate to be 1st and 2nd order in the NO concentration and the Cu^{2+} fraction, respectively [2]; b) the OHC rate to be 1st and 2nd order in the O_2 partial pressure (P_{O2}) and in the reduced Cu fraction, respectively.

Results and discussion.

By protocol (i) we monitored the temporal evolution of the Cu^{2+} fraction during Cu-oxidation (Figure 1A). Notably, O_2 alone was able to fully re-oxidize the catalyst after 1h at low temperature. The OHC data were nicely fitted by the assumed 2nd order redox kinetic model in Cu^{+}, confirming the oxidation half-cycle to be a dual-site mechanism with O_2 as the sole oxidant and an inconsequential role for NO [1]. Concerning the RHC, results from protocol (ii) confirmed the ability of NO+NH_3 to completely reduce Cu^{2+} sites to Cu^{+} producing N_2 according to a Cu^{2+}:NO:N_2=1:1:1 stoichiometry (Figure 1B). Again, the accuracy of the fit confirmed the 2nd order dependence of the reduction rate on the Cu^{2+} fraction [2]. These results emphasize the dominance of dinuclear Cu species in the redox mechanism of low-T Standard SCR. Once OHC and RHC were independently investigated, the estimated rate constants were used to directly predict the Standard SCR profiles from protocol (iii). Notably, the model was able to predict not only the steady state deNOx activity, but also the bed-average Cu^{2+} fraction at STD-SCR conditions, as well as the monotonic transient behavior of the NO/N_2 concentrations profiles (Figure 1C). The present results provide a stoichiometrically and kinetically consistent closure of the Cu redox cycle (with an overall NO:Cu=1:1 stoichiometry) in the STD-SCR chemistry and offer new insights into the LT NH_3-SCR mechanism over Cu-CHA.

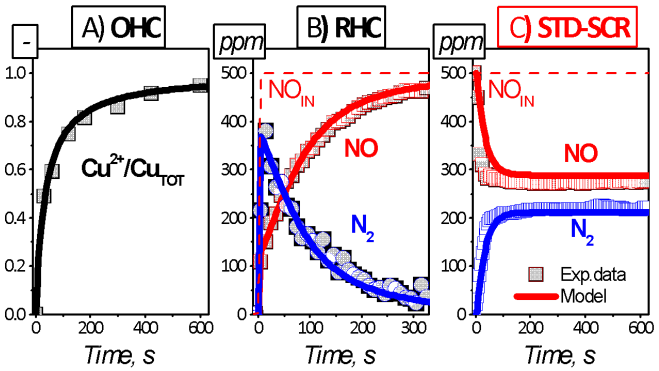

Figure 1: A): OHC: Cu^{2+} fraction B) RHC: NO,N_2 dynamics; C) STD-SCR: NO,N_2 dynamics. 200°C, 450000 Ncc/h/g_{CAT}

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Experimental and modelling analysis of the Standard SCR mechanism over Cu-CHA catalysts: SAR and H_2O effects on RHC and OHC

N.D. Nasello[1], N. Usberti[1], U. Iacobone[1], I. Nova[1], E. Tronconi[1*]
R. Villamaina[2], M.P. Ruggeri[2], D. Bounechada[2], A. York[2]

[1]*Laboratory of Catalysis and Catalytic Processess, Politecnico di Milano, Milano, Italy*
[2]*Johnson Matthey, Sonning Common, Reading, United Kingdom*
[*]*enrico.tronconi@polimi.it*

Keywords: Cu-zeolite, NH_3-SCR, redox mechanism, SAR effect

Introduction. NH_3-SCR (Selective Catalytic Reduction) over Cu-exchanged zeolite catalysts is considered the leading technology able to control the emission of nitrogen oxides (NOx) from Diesel engine exhausts [1,2]. Despite the high number of publications related to this topic, the low temperature mechanism (≤250°C) of the Standard SCR reaction is still highly debated [1-3]. Nowadays, there is a general consensus about the involvement of Cu in a cyclic redox mechanism, with its oxidation state varying from Cu^{II} to Cu^{I} and from Cu^{I} to Cu^{II} in the reduction (RHC) and oxidation half-cycles (OHC), respectively [1-3]. However, a clear understanding of the effects of the catalyst formulation (*e.g.*, SiO_2/Al_2O_3 ratio, SAR, and Cu loading) and of the gas feed composition (*e.g.*, NO, NH_3, O_2 and H_2O concentrations) on the SCR redox chemistry is still lacking. Herein, based on transient experiments and a kinetic modelling approach, we provide fundamental insights into the low-T Standard SCR mechanism, mainly focusing on the effects of SAR and H_2O.

Experimental/methodology. The study was performed over two model Cu-CHA catalysts (32 mg of powder) with same Cu loading (1.77% w/w) and different SAR (13 and 25). Dry and wet conditions (0-2% v/v H_2O) were investigated in a low T-range (150-200°C) according to three main protocols: i) isothermal reduction of a fully preoxidized catalyst with 500+500 ppm of $NO+NH_3$; ii) isothermal oxidation of a fully prereduced catalyst with 8% v/v of O_2 as the sole oxidant; iii) O_2 feed step changes from pure reduction ($NO+NH_3$) to Standard SCR ($O_2+NO+NH_3$) conditions, and vice versa. The collected data were further analyzed according to a transient integral model of the test flow reactor (cascade of 20 CSTRs) based on the following assumptions: i) 1st and 2nd order dependence of RHC rate on NO concentration and oxidized Cu fraction; 1st and 2nd order dependence of the OHC rate on O_2 concentration and reduced Cu fraction.

Results and discussion. According to protocols (i) and (ii), we confirmed on both samples: i) the ability of $NO+NH_3$ to completely reduce Cu^{II} sites; ii) Cu^{I} sites to be fully oxidized by O_2 as the sole oxidant. In addition, the good match between model and experimental profiles confirmed the accuracy of the assumed reaction pathways and kinetics of both RHC and OHC. Furthermore, the independently estimated RHC and OHC kinetic constants were able to successfully predict both NOx conversion and bed-average Cu^{II} fraction observed from protocol (iii) at STD-SCR steady-state. To evaluate the effect of SAR, the estimated rate constants (k_{RHC} and k_{OHC}) were compared in terms of Arrhenius plots over the two samples. For the sake of simplicity, only results for wet conditions are here described. In particular: i) higher k_{RHC} and apparent activation energy (E_{act}^{RHC}) were estimated over SAR13; ii) the opposite trend was observed for OHC, with k_{OHC} values and activation energy (E_{act}^{OHC}) higher on SAR25. Notably, H_2O showed the same kinetic effects of SAR, promoting OHC but inhibiting RHC [3], hence suggesting a possible correlation between SAR and H_2O effects: due to the less *hydrophilic* nature of the high-SAR zeolite, H_2O would be able to interact more intensely with the Cu cations, thus enhancing the OHC promotion as well as the RHC inhibition.

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Catalytic Activity and the Impact on Emissions: Fe-FER vs Fe-ZSM5

F. Oldani[1*], P. Biasi[1], R. Lanza[2], E. Rohart[3], A. Lahougue[3], A. Garbujo[1]

[1]*Casale SA, Lugano, Switzerland*
[2]*Verdant Chemical Technologies AB, Stockholm, Sweden*
[3]*Alsys, Ploemeur, France*
[*]*Corresponding Author's E-mail address: f.oldani@casale.ch*

Introduction.

Nitric acid is one of the most widely produced commodity in the world with approximal 60 million of tonnes produce annually [1] [2]. The production of nitric acid is coupled with the formation of nitrogen oxide and N_2O which is the third most impacting greenhouse gas (GHG) after CO_2 and CH_4. A catalytic abatement system is required to treat the flue gas of a nitric acid production plant, which is currently implemented using various catalytic systems. Fe-exchanged zeolites catalysts are currently the state of art catalysts which could achieve both NO_x and N_2O abatement. Many Fe zeolites have been explored, such as Ferrierite (FER), ZSM5 and BEA [3]. In this contribution, a comparison was made between fresh and aged Fe-FER and Fe-ZSM5 industrial catalysts, both supplied by ALSYS, in order to study the catalyst at the end of its operating life. Fe-FER catalyst is a proprietary catalyst of CASALE and ALSYS and it is used in nitric acid plants [4]. Field and laboratory results have shown that Fe-FER might allow customers to benefit from high catalytic activity and stability to lower catalyst turnover.

Experimental/methodology.

Commercial extruded catalysts were prepared on an industrial scale by ALSYS. The catalysts show a uniform cylindrical shape with a diameter close to 2 mm. Fe-FER and Fe-ZSM5 were subjected to a simulated accelerated ageing procedure, developed to model specific catalytic ageing, to study catalytic behavior at the end of the catalyst's life. Particular attention was devoted to the N_2O abatement. In fact, the catalytic tests were performed under relevant industrial in an Inconel reactor (deN_2O reaction condition: NO 70 ppm, NO_2 30 ppm, N_2O 900 ppm, O_2 3.0%, H_2O 0.3% and N_2 balance; deNO_x condition: NO 325 ppm, NO_2 325 ppm N_2O 40 ppm, NH_3 650 ppm, O_2 3.0%, H_2O 0.3% and N_2 balance.). A very high spatial velocity was used to highlight the differences in catalytic activity between the catalysts tested. Ageing treatments were carried out for 150 h at two temperatures (600 and 700°C) with 12% O_2 and 6% H_2O. The detector used was FT-IR coupled with a lambda probe for oxygen measurement.

Results and discussion.

Focusing on the fresh catalyst, the results show the higher catalytic activity of Fe-FER compared to Fe-ZSM5 for both NO_x and N_2O abatement. The superior catalytic activity of Fe-FER for N_2O abatement becomes particularly significant after the ageing procedure, where a different catalytic behaviour is observed. The results of the laboratory were used to analyse the impact of tertiary abatement catalyst on the nitric acid process performance, in terms of abatement system design and stack emissions. In addition, the study will contribute to the understanding of catalyst performance during the Start Of Run and End Of Run which are essential aspects for reducing overall emissions (NO_x and N_2O), achieving a more efficient process and minimising abatement system costs. The global GHG emissions over tertiary catalyst lifetime were evaluated for a typical nitric acid dual plant. The total catalyst volume used for emissions mitigation has been estimated for both catalysts considering the different deactivation behavior tested in laboratory. The reactor design based on Casale proprietary axial-radial gas flow through catalyst beds is shown as robust technology able to reduce overall installed catalyst volume by 5 – 10% with pressure drop across catalyst bed of 90 – 150 mBar and homogeneous gas distribution in the catalyst bed.

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Insight into the Effects of Dopants (Fe, Al) on Catalytic Performance and SO_2 Tolerance of MnO_x Catalysts for Low-Temperature NH_3-SCR of NO_x

H. Li[1], L. Schill[1], R. Fehmann[1], A. Riisager[1*]

[1]*Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark*
[*]*ar@kemi.dtu.dk*

Introduction. Mn-based catalysts have attracted significant attention as alternatives to vanadium-tungsten-titania (VWT) catalysts in the selective catalytic reduction of NO_x with NH_3 (NH_3-SCR), due to their excellent low temperature (LT) activity and environmental benignity. However, pure MnO_x catalysts suffer from a narrow active temperature window, undesirable NH_3 oxidation at relatively high temperature (>200 °C) and high sensitivity to H_2O and SO_2 [1,2]. In this work, the effects of co-metals (Fe and Al) as well as synthesis method on the catalytic performance, SO_2 resistance and regenarability of MnO_x catalysts were systematically studied.

Experimental/methodology. $MnFeO_x$ and $MnAlO_x$ were prepared by both the citric acid method (CA) and by a novel solvothermal method (H) and characterized by transmission electron microscopy (TEM) and temperature programmed reduction of H_2 (H_2-TPR). NH_3-SCR activity was tested in a fixed-bed quartz reactor at a weight hourly space velocity (WHSV) of 240,000 mL/(g·h) using a feed gas containing 600 ppm NO, 600 ppm NH_3, 4.5 vol.% O_2, 25 ppm SO_2 (when used), 2.5 vol.% H_2O (when used) and N_2 as the balance. S-poisoned samples were obtained by pre-treating catalysts with 100 ppm SO_2, 4.5 vol.% O_2 at 150 °C for 6 h. Catalyst regeneration was performed by heating in air at 400 °C for 2 h.

Results and discussion. $MnFeO_x$-H catalyst with a hybrid structure of nanoparticle and nanotube (Fig. 1a) showed better H_2O and SO_2 resistance than $MnFeO_x$-CA catalyst (Fig. 1b). The influence of Fe and Al on the performance of MnO_x catalyst was studied next (Fig. 1c). The NO_x conversion of $MnFeO_x$-H was ≥ 90 % at 100 to 250 °C, which is a wider temperature window than that of $MnAlO_x$ (150-250 °C). The NO_x conversion over both S-poisoned catalysts decreased significantly at low temperatures. However, $MnFeO_x$-H-S exhibited a higher NO_x conversion than $MnAlO_x$-H-S. After thermal regeneration, the activity of $MnFeO_x$-H-R was well recovered, which could reach 80% at 200 °C much higher than that of $MnAlO_x$-H-R (40%). Above all, $MnFeO_x$-H exhibited better LT activity, stronger SO_2 resistance and better thermal regeneration than $MnAlO_x$-H. H_2-TPR results (Fig. 1d) showed that the Fe doped catalysts were reduced at lower temperatures than Al doped counterparts, which could be due to the coordination between Mn and Fe through the redox cycles of $Mn^{4+}/Mn^{3+}/Mn^{2+}$ and Fe^{3+}/Fe^{2+}. Especially after regeneration, the coordination between Mn and Fe could help more Mn^{2+} to recover to Mn^{4+} and Mn^{3+}, resulting in a better performance than $MnAlO_x$-H-R.

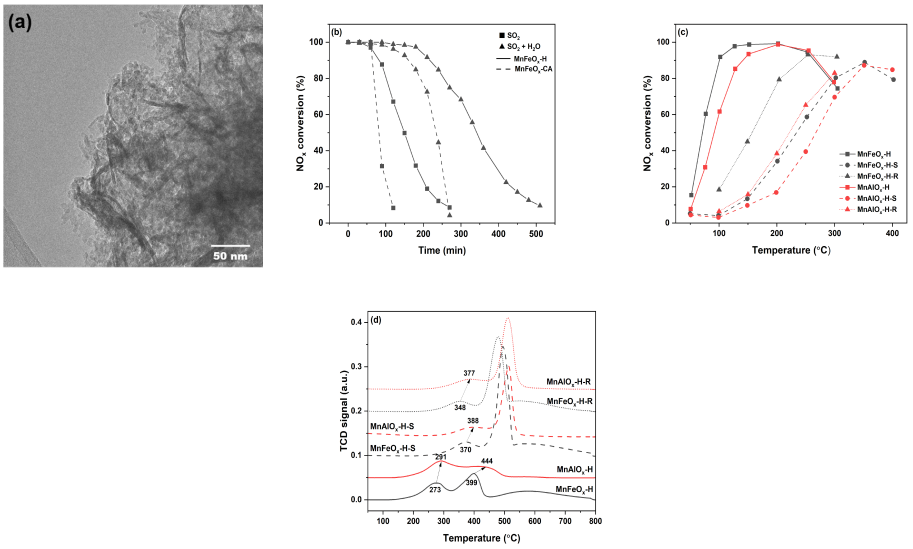

Fig 1. (a) TEM image of $MnFeO_x$-H catalyst, (b) SO_2 and H_2O tests of $MnFeO_x$-H and $MnFeO_x$-CA, (c) NO_x conversion of $MnFeO_x$-H, $MnAlO_x$-H and derived catalysts, (d) H_2-TPR of catalysts

Acknowledgements

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Investigation on Fe active sites in Fe/CHA catalysts for NH_3-SCR by Transient Response Methods

Maria Elena Azzoni[1], Isabella Nova[1], Enrico Tronconi[1]*,
Roberta Villamaina[2], Maria Pia Ruggeri[2], Veselina Georgieva[2], Loredana Mantarosie[2], Jill Collier[2]

[1]*Dipartimento di Energia, Politecnico di Milano, Milano, 20156 (Italy)*
[2]*Johnson Matthey Technology Centre, Sonning Common, Reading RG4 9NH (UK)*
[*]*enrico.tronconi@polimi.it*

Keywords: Fe-zeolite, NOx, Speciation

Introduction. The abatement of NOx and N_2O emissions from Diesel vehicles, due to increasingly strict regulations, represents an important challenge for the automotive sector**.** Whereas Cu/CHA catalysts are extensively employed for NH_3 SCR, Fe/CHA are now being investigated for their greater N_2O abatement activity and higher selectivity at high temperatures, compared to copper chabazites. While there is general agreement on the redox nature of NH_3-SCR mechanism, in which Fe ions cycle between Fe^{2+} and Fe^{3+}, the discussion on the nature of the active species and their role in the ammonia SCR chemistry is still open. The presence of different iron species in the catalyst complicates the rationalization of the results obtained with characterizations techniques (ex. UV-vis, Mossbauer) [1]. Transient response methods are here innovatively proposed as an additional methodology to improve the understanding of Fe/CHA catalysts. Specifically, given the important role of NO_2 in the SCR chemistry over Fe zeolites, we study the interaction between NO_2 and the Fe/CHA catalysts.

Experimental/methodology. Three Fe/CHA samples (Fe loading: 1%, 1.5 % and 3.0% w/w) are investigated. In the tests He is the carrier gas (GHSV=266250 Ncc/(h*gcat)) and the species concentrations are measured by an FT-IR gas analyzer and a Mass spectrometer. Two protocols are used: I) NO_2 adsorption + TPD: After a pre-oxidation with 8% O_2 v/v, 1 h at 550°C, NO_2 adsorption is performed at 150 °C (500 ppm of NO_2) then a Temperature Programmed Desorption is run (15°C/min, 150°C to 550°C), II) NO+NH_3 reduction: after a pre-oxidation step, 500ppm of NO and of NH_3 are fed to the catalyst at 330°C. NO+NH_3 reduction tests, succesfully employed for Cu/CHA [2], are performed in this study to investigate the oxidation state of the catalyst: firstly, after a pre-oxidation step at 550°C with 8% O_2 v/v; secondly, after preoxidation with 8% O_2 v/v and 500ppm of NO_2. It has been highlighted in previous works that NO_2 plays an important role in the SCR chemistry of Fe zeolites, since it is responsible for the greater activity of the Fast SCR with respect to the Standard SCR and is considered involved in the re-oxidation of isolated iron sites [1]. To investigate this aspect and elucidate the relation between the different Fe active species and their interaction with NO_2 the evolution of NO and N_2 during NO+NH_3 reduction tests is observed.

Results and discussion. The results show that the amount of released NO_2 during the TPD is proportional to the amount of Fe in the sample, in fact a ratio $NO_{2\ ads}/Fe_{load}$ of 2 between the amount of NO_2 adsorbed on the catalyst and the total amount of iron present in the sample is observed. Moreover, comparing the NO+NH_3 reduction tests performed for each sample, it is evident how the pretreatment with O_2 + NO_2 at 550°C leads to higher NO consumption/N_2 production, which can be rationalized as an increase in the oxidation state of the catalyst. Notably, the observed higher NO consumption cannot be due to the presence of NO_2 either in the gas mixture or prestored onto the catalyst surface, since the nitrogen dioxide is only fed during the pre-oxidation step at high temperature. A possible explanation for the stronger initial oxidation (i.e., with O_2 only or O_2+NO_2) is that NO_2 activates specific Fe species (e.g., isolated iron sites [1]) which cannot be oxidized in its absence.

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Kinetic Study by Energy Dispersive EXAFS on Cerium based Oxygen Storage Materials for Emission Control Catalysis

H.Gu [1], S.Marlow[1], L.Kang[1], Y.Ren[1], Z.Wang[1], X.Guan[1], H.Asakura[2],R.Wang[1*]

[1] *Department of Chemical Engineering, University College London, London, UK*

[2]*Faculty ofScience and Engineering, Kindai University, Osaka, Japan;*

[*]*ryan.wang@ucl.ac.uk*

Keywords: Ce based OSMs, Time-resolved Energy dispersive EXAFS, Emission control catalysis

Introduction. Oxygen releasing and storage are occurred by Ce(III)-Ce(IV) redox. Since oxygen storage reaction is very fast and real-time measurement is difficult by gas phase anlysis, real kinetic results for OSC are still lacking. Here we provide a general strategy for OSC kinetic study by probing changes of Ce(III)-Ce(IV) via an operando energy dispersive EXAFS during Oxygen realseing process. In addition, this research reaveled the relation between doping metal and Ce based support which will make it possible for us to develop OSMs for low temperature applications and to design efficient catalysts for other oxidation reaction.

Experimental/methodology. Energy dispersive EXAFS was used to monitoring the oxidation state changing of Ce by time resolution of 2 seconds. Non-monochromatic X-ray by bent crystal (polychromator crystal) was focused on the beginning part of sample near the inlet and then diverged towards a position sensitive detector where beam position is correlated to energy. FReLoN detector was used to detect the diverged beam after the sample. Ce L3-edge was measured simultaneously. Pure $Ce_{0.5}Zr_{0.5}O_2$ (CZ); 0.6wt%Cu/$Ce_{0.5}Zr_{0.5}O_2$ (Cu-CZ) and 1wt%Pd/$Ce_{0.5}Zr_{0.5}O_2$ (Pd-CZ) were measured with temperature from 373K to 623K.

Results and discussion. With 1wt% of Cu disperied on CZ, the reduction depth and rate was improved. The activation energy of Ce reduction for CZ is twice as much as Pd-CZ and almost four times more than Cu-CZ which is only 36.58 kJ/mol. Due to the unique $[Cu(I)O_2]^{3-}$ generated during redcution, the reductio ability of the Ce was enhenced sigenificantly[1], which means higher oxygen storage capacity can be achieved. The reaction pathway was changed with Cu doping, this also gives one detailed explaination for the metal-support interaction in emission control catalysis .

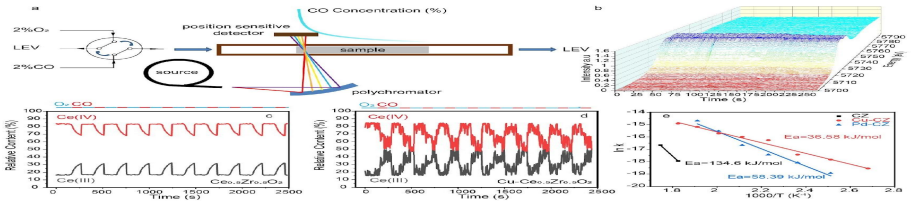

Figure 1. a Scheme of the experiment setup. b Evolution of Ce L3 edge XANES for CZ during fast gas switch. c,d Relative content for Ce during fast gas switch for CZ and Cu-CZ. e Arrhenius plot for CZ; Cu-CZ and Pd-CZ.

Acknowledgments. *We acknowledge Dimond Light Source for the operando EDE experiments conducted under proposal no.sp29201, and NEXAFS under proposal no.SI31012. We acknowledgede Spring-8 for the in-situ XAFS experiments under proposal no.2022B1857.*

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Ceria-Supported Metal Nanocatalysts for CO Abatement in Industrial Combustion Exhaust Gases

A. Lazzarini[1,*], L. Atzori[2], F. Ferella[1,3], M. Signorile[4], G. Cutrufello[2], E. Rombi[2], M. Crucianelli[1]

[1]*DSFC, University of L'Aquila, Via Vetoio (COPPITO 2), 67100, L'Aquila - Italy*
[2]*DSCG, University of Cagliari, S.S. 554 bivio Sestu, 09042, Monserrato (CA) - Italy*
[3]*INFN Gran Sasso National Laboratories, Via G. Acitelli 22, 67100, Assergi (AQ) - Italy*
[4]*Department of Chemistry, University of Torino, Via G. Quarello 15/A, 10135, Torino - Italy*
*****andrea.lazzarini@univaq.it*

Keywords: CO oxidation, active supports, nanostructured ceria, bi-metal catalysts.

Introduction. Air pollution has become one of the main environmental issues in the modern society. While for transportation very restrictive limitations on emission are already present, for industrial ones are expected to be adopted in few years, especially for CO emissions that will need to be cut below 500 ppm [1]. Pt-based catalysts are already largely employed for CO oxidation [2]; however, economical aspects cannot be neglected anymore. For such reason, we designed a ceria-supported catalyst based on more affordable metallic active phase, namely Fe, Ni, and Fe-Ni mixed phase [3].

Experimental. Soft-templated (CTAB) and hard-templated (SBA-15) ceria [4] were prepared and active metal phases were deposited by incipient wetness impregnation method, aiming to 5 $\%_{mol.}$; then, the materials were calcined in air at 600 °C for 3 h. The catalysts were then thoroughly characterized (BET, XRD, SEM, HR-TEM, EDX, ICP-MS, Raman, CO@FT-IR at 77 K) and then tested for CO oxidation.

Results and discussion. From preliminary catalytic screemning, we observed an extremely high activity of Pt catalyst (as expected), slightly lower for Ni catalyst, and almost no catalytic activity for the Fe one. Interestingly, Fe-Ni sample displayed activity close to Pt (> 99%, fulfilling the 500 ppm requirement) in the T range of our interest (300-400 °C), especially when supported on hard-templated ceria. Indeed, the growth inside SBA-15 channels gave 30% larger surface area to the support than CTAB did. XRD did not show any sign of NPs formation; Raman and CO@FT-IR spectroscopies evidenced the insertion of Ni^{2+} isolated species inside superficial defective sites of ceria supports. Such effect was enhanced by the presence of Fe, enhancing the exposure of Ni sites. Finally, the Fe-Ni hard-templated catalyst was tested in real conditions [5] for several days, maintaining a CO conversion > 97%. The slight deactivation was probed with CO@FT-IR and identified in the formation of a small fraction of Ni NPs.

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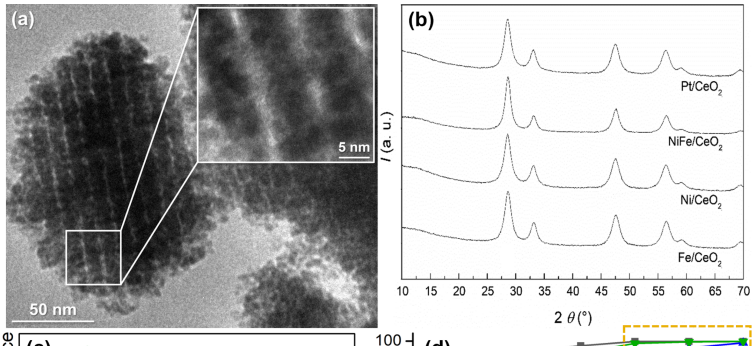

Distinct morphology-dependent behavior and reaction mechanism over $BaCoO_3/CeO_2$ catalysts for NO direct decomposition

Running Kang[1,2], Yongdan Li[1*]

[1] *Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Kemistintie 1, Espoo, P.O. Box 16100, FI-00076, Finland*

[2] *State Key Laboratory of High-Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China*

[*] *Corresponding author. Email: yongdan.li@aalto.fi (Y. Li)*

Keywords: NO direct decomposition; Perovskite; $BaCoO_3$; CeO_2 morphology; Reaction mechanism

1. Introduction. Nitrogen oxides (NO_x), emitted in the flue gas from stationary sources, is extremely toxic to human health and environment via forming acid rain, photochemical smog, and ozone layer depletion. Currently, several technologies have been proposed for NO_x abatement, such as selective catalytic reduction (SCR) with ammonia, selective non-catalytic reduction and NO_x storage and reduction, and etc. [1]. Among these technologies, NO direct decomposition ($2NO \rightarrow N_2 + O_2$) has been regarded as the most attractive pathway for NO removal due to its eco-friendly and no requirement of reductants [2,3]. However, its practical application is hampered by low activity and low O_2 resistance of the catalysts. Moreover, the research on distinct structure-activity relationship and detailed reaction mechanism with/no O_2 for NO direct decomposition are still unclear, and the design of high-performance catalyst is another bottleneck that restricts this technology.

2. Experimental/methodology. The $BaCoO_3/CeO_2$ catalyst samples were prepared with an excess impregnation method. The three samples by using different morphology of CeO_2 support, are referred to as $BaCoO_3/CeO_2$-particles (BCP), $BaCoO_3/CeO_2$-sphere (BCS), and $BaCoO_3/CeO_2$-rod (BCR). The XRD, N_2-BET, HRTEM, SEM+EDX, XPS, H_2-TPR, O_2/NO-TPD, *In situ* DRIFT and isotopic ($^{18}O_2$) exchange experiments were performed to investigate the structure-activity relationship and reaction pathways.

3. Results and discussion. The activity, NO conversion to N_2 at 800 °C follows an order $BaCoO_3/CeO_2$-r (78.8%) > $BaCoO_3/CeO_2$-s (75.9%) > $BaCoO_3/CeO_2$-p (56.9%)> $BaCoO_3$ (8.6%) at a space velocity 1 g·s/cm^3. The $BaCoO_3/CeO_2$-r exhibts high tolerance to O_2 and high stability with conversion decrease from 78.8% to 74.6%, 60.0% and 50.0% at 800 °C with 1, 5 and 10 vol% O_2, respectively. The high redox activity, higher active oxygen mobility and NO adsorption capability ensures the high activity, while the high surface area (31.29 m^2/g) and uniform distribution of active sites on the surface also promote the performance. Such superior catalytic activity and O_2 tolerance of BCR are attributed to the strong proveskite-support interaction (PSI) on the oxide phases interface. In situ DRIFT and $^{18}O^2$ isotopic transient exchange experiments reveal that the rate-determining step is the formation of N_2O*.

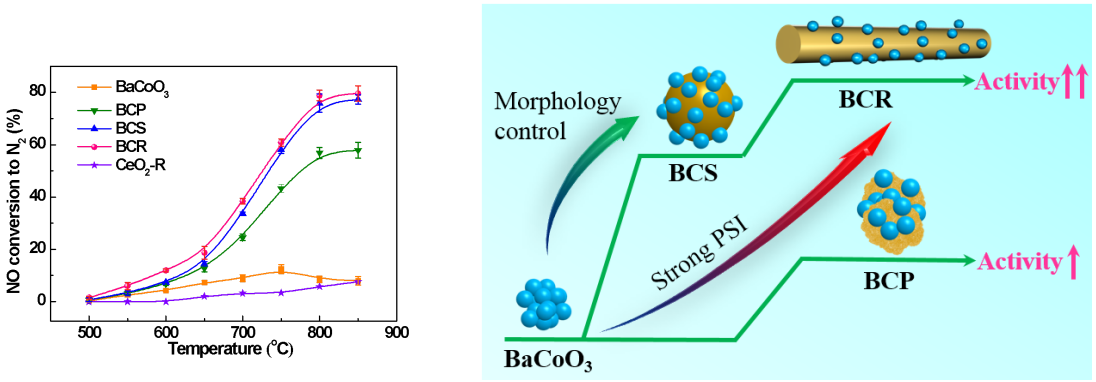

Fig.1. Activity results of catalysts and structure-activity relationship

Acknowledgments. *The authors gratefully acknowledge the financial support from the International Science and Technology Cooperation Projects (Sinopec. 410920).*

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Unravelling the structure and role of Mn and Ce for NOx reduction in aplication-relevant catalysts

Lieven Gevers[1], Linga Enakonda[1], Ameen Shahid[1], Samy Ould-Chikh[1], Cristina I.Q. Silva[1], Pasi P. Paalanen[1], Antonio Aguilar-Tapia, Jean-Louis Hazemann, Mohamend N. Hedhili[1], Fei Wen and Javier Ruiz-Martinez[1]*

[1] *KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia*

*javier.ruizmartinez@kaust.edu.sa

Introduction. Mn-based oxides are promising catalysts for the selective catalytic reduction (SCR) of NOx with NH3 at temperatures below 200 °C [1]. There is a general agreement that combining Mn with another metal oxide, such as CeOx improves catalytic activity. However, to date, there is an unsettling debate on the role of Ce as Mn promoter on the SCR reaction. To solve this, here we have systematically studied the effect Ce by preparing, characterizing, and testing around 30 catalysts aiming for a well-controlled homogeneous dispersion of the metal oxides.

Experimental/methodology. A series of individual, binary and ternary materials with different molar concentrations were prepared by a controlled co-precipitation method. Several characterization techniques were used, such as X-ray diffraction, N_2 physisorption at 77 K, elemental composition by inductive coupled plasma spectrometry, temperature-programmed reduction with H_2 and temperature-programmed desorption of NH_3, high-resolution X-ray photoelectron spectroscopy, X-ray absorption spectroscopy and annular dark-field scanning transmission electron microscopy in conjunction with electron energy-loss spectroscopy. The catalytic activity measurements in the NH_3-SCR reaction were carried out in a commercial PID reactor at conditions close to a real lean-burn diesel engine.

Results and discussion. Characterization strongly confirms that the synthetic route renders an amorphous and homogeneous distribution of all the metal atoms in the ternary Mn, Ce and Ti mixed oxides. This is also corroborated by high-resolution electron microscopy (figure 1a). XPS also confirms that surface and bulk compositions match. H_2-TPR suggest an interaction of Mn species with Ce, which increases the reduction temperature of Mn. The catalytic activity of the samples was measured at low temperature (150 °C). When activity was surface-area normalized, a clear linear dependency with the amount of Mn is observed in the binary Mn-Ti samples. The ternary Mn-Ce-Ti has also a pseudolinear correlation with the Mn content but with a lower slope (Figure 1b). We inferred that MnOx species in the binary Mn-Ti catalysts are more active than in the Mn-Ce-Ti catalysts and that Ce is just an structural promotor, increasing catalyst surface area. On the other hand, addition of Ce is increasing N_2 selectivity as it suppresses second step oxidation and thus N_2O formation by a dilution effect on the MnOx active sites [2] (see figure 1c and d) The latter still makes Ce an attractive additive for Mn-Ti systems.

Figure 1. a) Elemental mapping of a selected Mn-Ce-Ti catalyst in high magnification showing a homogeneous distribution of the different metal oxides. b) Surface-specific activities for the NO reduction at 150 °C plotted as a function of the Mn content on the catalysts. The blue dots correspond to the ternary Mn-Ce-Ti catalysts. The red dots are from the binary Mn-Ti and the individual Mn catalysts. c) Surface-specific N_2O rates at 150 °C as a function of the Mn surface density. d) Schematic representation of the reaction mechanism in a Mn-Ce-Ti ternary catalyst in which a well-mixed amorphous structure promotes the spacing of MnOx species and therefore reduces the formation of N_2O.

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Cu/CeO_2 catalyst for NH_3 formation from NOx using CO + H_2O as reductants

Y. Manaka[1,2*], K. Kobayashi[1], T. Nanba[1]

[1]*National Institute of Advanced Industrial Science and Technology, Koriyama, Japan*
[2]*Tokyo Institute of Technology, Tokyo, Japan*
[*]*yuichi.manaka@aist.go.jp*

Keywords: NOx, NH_3, Water-gas-shift reaction

Introduction. NOx emitted from combustor of power plant and mobile sources is known to be environmental pollutants. Selective catalytic reduction of NOx to N_2 by NH_3 has been investigated promising way to reduce NOx emission. We have been proposed that NOx should be converted to valuable materials rather than N_2 production.

We reported that Pt catalysts supported on TiO_2 showed high activity for NO to NH_3 reaction using CO + H_2O as reductant in the previous study[1]. Intermediate species of water gas shift reaction (WGS), such as formate, were involved in NH_3 formation on the NO-CO-H_2O reaction. Considering this finding, the catalysts having WGS activity would have a capacity to form NH_3 in NO-CO-H_2O reaction. Cu/CeO_2 is reported to show high activity for WGS reaction, we employed Cu/CeO_2 for NH_3 formation on NO-CO-H_2O reaction in this study[2].

Experimental/methodology. Copper catalysts were prepared by means of incipient wetness method. After 1, 3, 5, 10, 20 and 40wt% Cu loading, the sample was calcined at 773 K for 4 h, and then reduced under 10 vol%H_2/N_2 at 673 K for 1 hour. Catalytic activity test was performed using a fixed bed flow reactor. Sample was used 0.15 g. The concentration of NO-CO-H_2O reaction were 1000 ppm NO, 3000 ppm CO and 1% H_2O.

Results and discussion. Temperature dependence of Catalytic activity of 5wt% Cu/CeO_2 for the NO-CO-H_2O are shown in Fig. For NO-CO-H_2O reaction, NO conversion increased with increasing temperature, and then reached 100 % above 473 K. NO conversions to NH_3 were 68% and 83% at 423 and 473K, respectively. Above 473 K, NO conversion to NH_3 were in the range of 80-85%. N_2+N_2O concentrations were lower than 44 ppm, which was corresponding to NO conversion to N_2+N_2O of 4%, at all temperature measured. NO conversion to NH_3 on Pt/TiO_2 at 423 K was 61%, so that Cu/CeO_2 exhibited almost 10% higher value. Almost same NH_3 formation as Pt/TiO_2 was succeeded without using the precious metal.

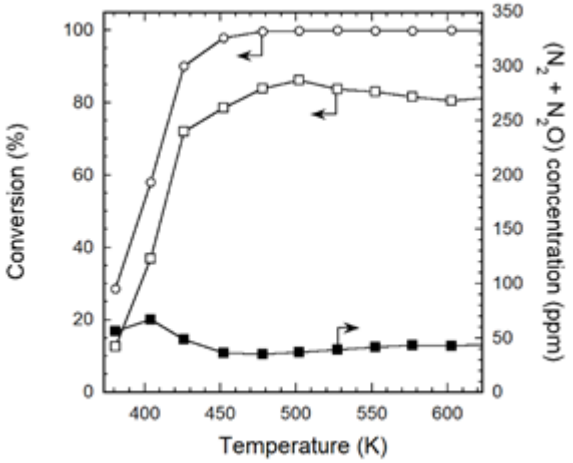

Fig. Catalytic activity of 5wt%Cu/CeO_2 catalyst under NO-CO-H_2O, (circle) NO conversion, (square) NO conversion to NH_3, (filled square) N_2 and N_2O concentrationtables

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Kinetics of site transformations in a Cu/SSZ-13 catalyst during aging

Tetyana Zheleznyak[1], Petr Kočí[1*], Kanika Meena[2], Lai Wei[3], William Epling[2]

[1]*University of Chemistry and Technology, Prague, Czech Republic*
[2]*University of Virginia, Charlottesville, USA*
[3]*Cummins Inc., Columbus, USA*
[*]*petr.koci@vscht.cz, www.vscht.cz/monolith*

Keywords: exhaust gas aftertreatment, selective catalytic reduction, NO_x, reaction kinetics

Introduction

Selective catalytic reduction of nitrogen oxides (SCR) using Cu ion exchanged into SSZ-13 zeolite, Cu/SSZ13, is the current standard technology for diesel engine exhaust NO emissions reduction. The active species start as ion-exchanged Cu, with 2 such sites often described, Z_2Cu and ZCuOH, where Z represents a zeolite Al site. However, a distribution of sites exists, including these two ion-exchanged Cu types, solvated Cu, as well as multinuclear Cu and CuO nanoparticles. Each of these plays a different role in desired and undesired reactions. The site distribution evolves with time on stream and reaction conditions, and therefore the model must evolve also. This means including rate laws for changes in active site concentrations as a function of reaction environment conditions.

Experimental methods

A commercial Cu-SSZ-13 SCR honeycomb monolith provided by Cummins Inc. was employed in the experiments. The migration of Cu species during hydrothermal aging, as well as the change in Cu distribution on low-temperature and high-temperature NH_3 oxidation and SCR reaction mechanisms are considered. The impact of sulfur oxides (SO_2 and SO_3) on the transformation processes is also investigated. Characterization techniques include H_2 temperature-programmed reduction (H_2TPR), NO+NH_3-TPR, NH_3 temperature-programmed desorption (NH_3-TPD), CO titration, and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) are used to characterize and quantify catalyst site densities. Based on the experimental data, kinetic equations for transformation rates for individual site types are expressed as functions of actual site concentration, gas composition and temperature.

Results and discussion

Cu migration occurs both from the ZCuOH to the Z_2Cu position, and from both ion-exchanged positions to agglomerated Cu particles. For the former, “mild” hydrothermal aging (HTA) conditions lead to such a transition. Changes in Z_2Cu and ZCuOH site numbers have been correlated to changes in Brönsted acid sites, as Z_2Cu requires 2 Al sites whereas ZCuOH only 1. The total amount of NH_3 desorbed remains constant, as does the total amount of ion-exchanged Cu measured in a separate experiment. But there is a shift in NH_3 desorbing at low versus high temperature, away from the high temperature associated with the Brönsted acid sites in the zeolite, to the lower temperature associated with the Lewis acid Cu site. The loss in Brönsted acid site number correlates directly to the amount of ZCuOH that transformed to Z_2Cu. In terms of Cu agglomeration into particles, higher temperatures induce this loss in SCR active species through the zeolite structure collapsing and Cu dissociation from the zeolite framework positions and subsequent agglomeration.

Acknowledgments

This work was financially supported by the National Science Foundation (NSF 2227016) and the Czech Science Foundation (GA 23-07137L).

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NO_x adsorption and stability on Pd/SSZ-13 low-T adsorbers: mechanistic pathways investigated by *Operando* FTIR spectroscopy

Y. Hamid[1], R. Matarrese[1], S. Morandi[2], L. Castoldi[1], L. Lietti[1*]

[1]*Politecnico di Milano, Dept. of Energy, Milano, Italy*
[2]*University of Turin, Dept. of Chemistry, Torino, Italy*
[*]*luca.lietti@polimi.it*

Keywords: Pd-doped zeolites, Cold-start, NOx adsorbers, PNA, Pd, SSZ-13, Operando FT – IR Spectroscopy.

Introduction. Significant amounts of NO_x are emitted during vehicle cold-start, since after-treatment devices like SCR and/or LNT systems are inactive at low temperature [1,2]. A possible solution is the adoption of low temperature NO_x adsorbers, the so-called Passive NOx Adsorbers (PNAs) that utilize their ability to temporarily store NO_x at low temperature (<150 °C) and release at higher temperature. The use of Pd-promoted zeolites has been suggested, which however must be optimized in view of the high cost of the active Pd component. Goal of this study is to deepen mechanistic aspects related to the low-T adsorption/desorption of NO_x and to envisage by means of *Operando* FT- IR Spectroscopy and microreactor studies the role of species like CO, HC, O_2 and H_2O on the performance of catalyst .

Experimental/methodology. An home-made Pd-doped chabazite sample (Pd loading 1% w/w), calcined at 750°C has been considered in this study. NO_x adsorption experiments were conducted both in a microreactor apparatus and in an *operando* FT-IR apparatus at different temperatures; the thermal stability of the NO_x stored species has been investigated by temperature programmed desorption (TPD). Experiments have been done in presence/absence of CO, C_3H_6, H_2O and O_2.

Results and discussion. Catalyst characterization indicates the presence of isolated Pd species (with oxidation states +1 and +2) and (minor) PdO particles as well. Upon NO_x adsorption the formation of Pd^{n+} nitrosyls , in the form of anhydrous or hydrated complexes depending on the adsorption temperature (bands in the range 1750-1850 cm^{-1}) is observed, involving Pd^{2+} to Pd^{+} sites. Nitrosyls formation is accompanied by NO_2 evolution, and possibly by the reduction of Pd^{2+} to Pd^{+}. Bands related to monodentate and bidentate nitrates (1330 and 1457 cm^{-1}) were apparent as well when adsorption is carried out at low temperatures. Upon heating the sample (see Fig. 1a as example), hydrated nitrosyls transform into anhydrous nitrosyls (bands at 1810 and 1850 cm^{-1}) below 200°C, and desorption of water is observed. Nitrates also decompose at these temperatures. Anhydrous nitrosyls show much higher thermal stability and decompose above 300°C (Fig. 1c). When CO is present in the feed, Pd-carbonyls and -nitrosyls are formed, but the displacement of carbonyls by nitrosyls is observed. However CO reduces the Pd sites and modify the NO adsorption. Similar effects have been observed in the case of C_3H_6, although in this case the hydrocarbon molecule is not easily displaced by NO.

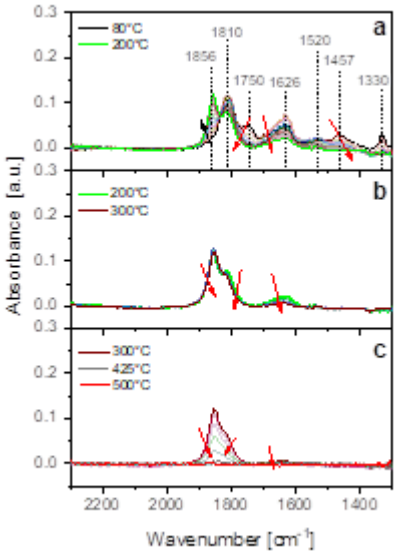

Fig 1. FTIR spectra recorded upon heating the Pd/SSZ-13 sample after NO adsorption at 80°C in the presence of O_2 and H_2O

The impact of O_2 and H_2O on the pathways involved in NOx adsorption/desorption have also been analyzed. Oxygen alone has a minor effect on the catalyst's adsorption capacity and on the stability of the nitrosyls, while water slightly modifies the NO storage capacity but greatly modifies the thermal stability of the adsorbed species.

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Phosphorous contamination of a V/W-TiO2 Monolith Catalysts used for NH_3-SCR of NO_x in bio-fuel combustion exhaust

Silje F. Håkonsen[1]*, Martin F. Sunding[1], Bjørnar Arstad[1], Anna Lind[1], Jasmina H. Cavka[1], David Waller[2], Karl Isak Skau[2]

[1]*SINTEF Industry, Forskningsveien 1, 0373 Oslo, Norway*
[2]*Yara International ASA, Yara Technology Centre, P.O. Box 1130, 3905 Porsgrunn, Norway*
[*]*Siljefosse.hakonsen@sintef.no*

Keywords: SCR, catalyst deactivation, phosphorous

Introduction. Emission of nitrogen oxides (NO_x) is regarded as a major source of atmospheric pollution and must be kept at a minimum. Selective catalytic reduction (SCR) catalysts are commonly used for NO_x emission reduction but with the increase in bio-based fuels for engines and in incineration processes, phosphorus contamination is more common compared to processes utilizing fossil-based fuels. In this work we have studied commercial V_2O_5-WO_3/TiO_2 monolith catalysts that have been exposed to bio-based fuel during incineration for two different periods of time in a commercial system.

Experimental/methodology. In this study we have performed characterization of a fresh unused monolith sample and compared it with samples collected from the monoliths used in a commerical plant for different time on streams utilising a range of methods: Temperature programmed desorption of ammonia (NH_3-TPD), X-ray photoelectron spectroscopy (XPS) and activity measurements.

Results and discussion. Samples were extracted from the used monoliths and the most significant finding regarding impurity elements was the increasing amount of phosphorous with time on stream, together with a lower activity regarding NOx conversion. Other elements showed a rather small or insignificant change with use for these samples. The phosphorous species were found to be of the phosphate types and the Brønsted site density and apparent strength was similar to the native catalyst. XPS data indicate that the oxidation state of V has changed in contrast to W, which remained the same. A lock of V into an oxidation state of +IV, not suited for the operating red-ox cycles, is detrimental to activity. Figure 1 shows the concentration of elements measured by EDS profiles of the cross section of the catalyst monolith walls.

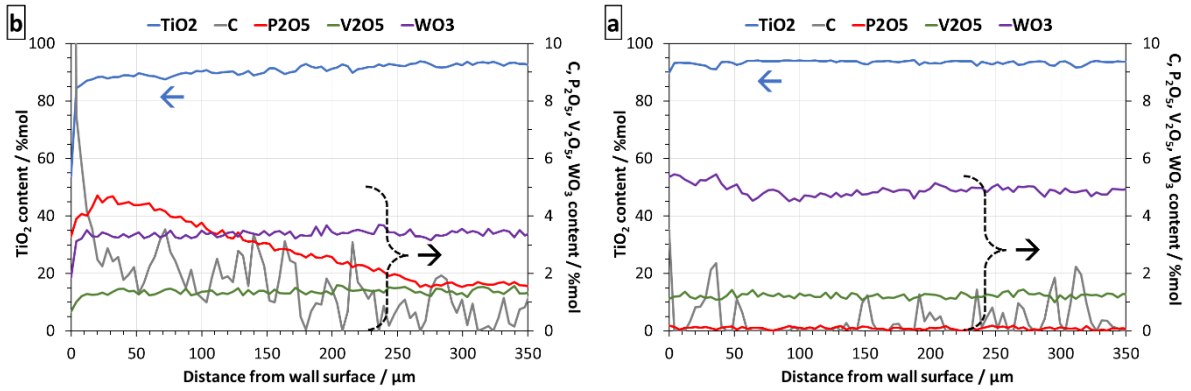

Figure 1: EDS composition profiles for the catalyst material as well as carbon and phosphorous, from edge to centre of the catalyst monolith wall; a) fresh catalyst and b) used catalyst.

Acknowledgments

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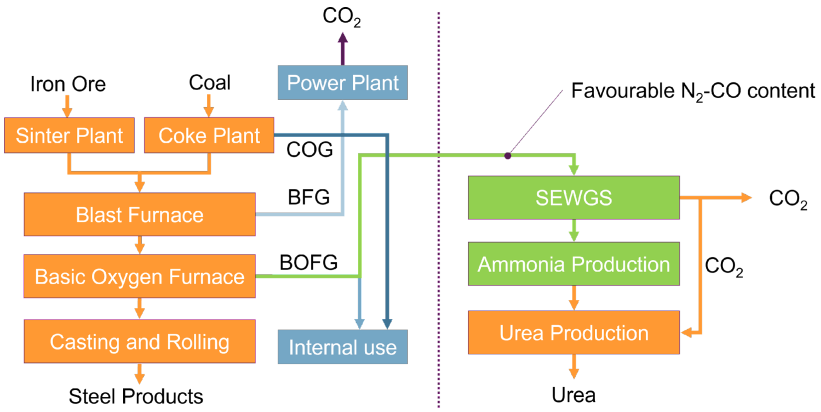
Valorising Emissions from Steel Making into Sustainable Products

Liliana Lukashuk[1*], Santiago Palencia Ruiz[1], H.A.J. van Dijk[2]

[1]*Johnson Matthey, Billingham, UK*
[2]*TNO, Petten, the Netherlands*
[*]*liliana.lukashuk@matthey.com*

Introduction

To reach EU climate targets, the steel and iron production sectors are looking to decrease their CO_2 emissions by up to 90% by 2050. The INITIATE project aims to demonstrate how residual carbon-rich gases, such as blast furnace gas (BFG) and basic oxygen furnace gas (BOFG), from the steel sector can become a valuable feedstock for the chemical sector, leading to a cost-efficient decarbonisation of the steel industry.[1] The demonstration includes the continuous production of N_2+H_2 and CO_2 streams (i.e., a feedstock for the ammonia and urea industries), reducing the overall carbon footprint. The project aims at a 30% decrease of primary energy use, a 40% decrease of raw material demand and up to 90% reduction in the direct CO_2 emissions. The INITIATE project takes all necessary steps to provide the basis for the roll-out of a 1st commercial size demonstrator at 50 kt/y urea on the basis of BOFG.



Experimental/methodology

The design of the pilot plant, which will be constructed at the partner SWERIM's site in Lulea, Sweden, is nearing completion. The pilot will take BFG and BOFG from the SSAB steel plant next-door, decarbonise it, tune the H_2/N_2 ratio of the intermediate product and produce NH_3 at TRL-7 scale. For the novel concept of BOFG to ammonia, the functional materials (i.e., water gas shift (WGS) catalyst to produce hydrogen from BOFG; materials for the removal of sulphur species and CO + CO_2 to purify the hydrogen stream for ammonia production) are currently being defined and evaluated at lab-scale.

Results and discussion

In the INITIATE project, the WGS section is an essential part of the technology where CO-rich gases are converted to hydrogen and CO_2. We have demonstrated previously the suitability of the iron-based HTWGS catalyst for the production of hydrogen from BFG streams.[2] An advanced split-flow WGS configuration will be deployed to produce hydrogen from industrial residual gases from the iron and steel industry at pilot plant scale. This WGS concept allows to optimise the steam requirement, contributing to minimise the energy penalty associated with the novel CO_2 removal.[3] An important aspect is the identification and quantification of the contaminants present in the BFG and BOFG, as it influences the functional materials choice and pilot lay-out. In parallel to a literature review, extensive contaminant measurement campaigns were performed at SSAB for BOFG. This resulted in a detailed overview of the type and level of contaminants that may be expected and the definition of the pilot clean-up section upstream the ammonia loop. The findings emphasise the need for tailored investigations per site as the gas composition can vary significantly.

Acknowledgments

This work is part of the INITIATE project that has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N°958318.

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Aging of Three-Way Catalysts for Biogas Fuelled Heavy-Duty Trucks

Anders Ersson[1]*, Samuel af Ugglas[1,2], Maximilian Kempe[1,2], Moa Sundén[1], and Henrik Kusar[2]

[1]*Scania CV AB, Södertälje (Sweden)*
[2] *Department of Chemical Engineering, KTH – Royal Institute of Technology, Stockholm, (Sweden)*
[*] *anders.ersson@scania.com*

Keywords: Three-way catalysts, biogas, heavy transport, aging

Introduction. Biogas as fuel for heavy transport have become a very good alternative to conventional diesel. The biogas, which can be produced from a large variety of wastes, is considered a very beneficial biofuels from a greenhouse gas perspective [1]. The biogas is most commonly used as a fuel in Otto type engines where three way catalysts, TWC, is the preferred exhaust treatment solution. Even though TWC:s have been around for a long time for gasoline cars. The use for heavy-duty trucks and the use of gaseous fuels, mainly consisting of methane puts new demands on the TWC catalysts. For example the unburnt methane from the fuel is much more difficult to oxidize compared to the unburnt hydrocarbons from gasoline engines [2].

The TWC in heavy trucks have significantly higher demands on life lengths compared to gasoline fuelled passenger cars, which increases the demand for high resilience towards aging for TWC used in heavy duty applications.

In the present study catalyst samples subjected to accelerated hydrothermal aging were compared to aged catalysts samples from real life vehicles. The material properties as well as the catalytic activity were used for the comparison.

Experimental/methodology. Seven catalytic samples were retrieved from a fresh, commercially available three-way catalyst. Six of the samples were aged in a gas-flow reactor where the O_2 concentration, temperature, and time were changed. The activity of the aged and fresh catalyst samples were evaluated in a synthetic catalytic activity test reactor (SCAT) at different static light-off conditions. The results were compared to a number of aged samples from actual trucks.

Results and discussion. The main objectives of the study was to compared accelerated hydrothermal aging in labscale environment with the aging of real field TWC samples. The study have shown that the lab-scale aging affected both the CH_4 oxidation and the reduction of the NO_X with tests of field age samples. The ongoing work will compare these results with the result for several field aged samples from biogas fuelled heavy duty trucks.

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The Effect of Various Renewable Fuels on Diesel Particulate Filter Performance

S. af Ugglas[1,2*], A. Ersson[1], L. J. Pettersson[2], H. Kusar[2]

[1]*Scania CV AB, Södertälje, Sweden*
[2]*KTH Royal Institute of Technology Chemical Engineering, Stockholm, Sweden*
[*]*samuel.af.ugglas@scania.com*

Introduction

The use of fuels derived from renewable sources is increasing in the pursuit of reducing the impact on climate and fossil dependency of the transport sector [1]. However, the use of biofuels changes the composition of the exhaust gases and can introduce impurities posing new challenges to the exhaust aftertreatment system [2]. Alkali metals present in the exhaust are known to poison the automotive catalysts and also form ash with other properties compared to lubricant-derived ash which further impacts the performance of the diesel particulate filter [3, 4].

Experimental

Catalytic diesel particulate filters have been collected from heavy-duty vehicles running on various renewable fuels and blends. Evaluation of the catalytic activity towards NO and HC oxidation was performed with a gas flow reactor connected to a continuous gas analysis equipment. Assessment of the aging is performed by correlating the physicochemical properties to the catalytic performance of the samples.

Results and discussion

Chemical poisons can be found in various degree for all samples. While the level of poisons appears to be less dependent of kilometers driven, the amount of Na and K are strongly correlated to the composition of the fuel used during operation. Assessment of the samples indicates excessive aging of the samples with higher alkali metal content leading to a decrease in the catalytic activity.

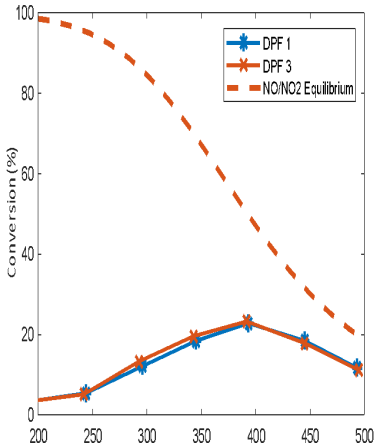

Figure 1. Oxidation of NO at 50 000 GHSV in 6 vol% O2, 5vol% H2O, 600 ppm NO and 300 ppm C3H8

Acknowledgments

This work is part of the project "Future Particulate Filters for Next Generation Biofuels", sponsored by the Swedish Energy Agency – FFI program and supported by Scania CV AB, Department of Chemical Engineering, Johnson Matthey and RenFuel K2B AB. The authors are grateful for all participants' contributions.

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Doped Ceria Catalysts for NOx Storage and Reduction

O. Hamill[1], A. Goguet[1], N. Collis[2], P. Millington[2], J. Collier[2], L. Mantarosie[2], N. Artioli[*]
[1]*Queen's University Belfast, Belfast, United Kingdom*
[2]*Johnson Matthey Technology Centre, Reading, United Kingdom*
[*]*n.artioli@qub.ac.uk*

Keywords: Doped Ceria, NOx Reduction, Emission Control

Introduction:

The new Euro 7 protocol, proposed by the Commission on 26th October 2022, concerning emissions of lean-burn engines, presents a need for further optimisation of existing after-treatment technologies. It reveals a 35% reduction to the NOx emission limit for cars and vans, compared to Euro 6 [1]. A well-known technology employed to reduce NOx to clean emissions in light-duty vehicles is the Lean NOx Trap (LNT). LNTs employ catalysts consisting of PGMs supported on ceria (CeO_2) or other mixed oxides. Ceria's redox property makes it an attractive selection, as well as its ability to store NO_x at low temp (<300 ˚C), especially when Pt is present. Storage properties of ceria can be further enhanced by doping. Dopants reportedly allow ceria to function better at low temperature (<300 ˚C), and to reduce the PGM loading required to achieve the same conversion efficiencies. [2] The RE metals Sm, Pr and Nd have been employed as dopants on CeO_2 for LNT applications to increase surface oxygen content, oxygen vacancies, defect densities, and cause changes to the Pt-ceria interaction. These structural changes can allow for higher NSC during lean operation and enhanced activation during rich purge. [3] Sm, Pr and Nd doped catalysts (10 wt.%) were synthesised on a range of ceria based catalysts with different Pt loadings (0-1 wt.%). Morphological changes observed through dopant addition has been investigated and related to catalytic performance increases.

Experimental/methodology:

NOx Storage Capacity experiments were carried out in a fixed bed reactor (tot. flow 200 Ncc/min, 40mg cat). Initial activation and cleaning ran from RT to 450˚C flowing 0.4% H_2 in Ar. Storage conditions consisted of 5% O_2, 400ppm NO, balanced with Ar. For H_2-TPR experiments; catalysts were pretreated to 500°C for 1hr in 10% O_2/He (35ml/min). H_2 consumption was measured from 0-1000°C in 5%H_2/Ar (35ml/min) at 10˚C/min.

Results and discussion:

NSC experiments were performed to assess the differences in NO_x storage capabilities at low temperatures (150-300˚C), on a range of doped ceria and Pt-ceria samples (Figure 1). It is observed that, at 150˚C, the NSC increases by 15% and 40% compared to that of the bare support, upon doping with Sm and Pr, respectively. To understand the dopant effect on NOx storage and oxidation capability, H_2-TPR experiments were also performed. Figure 2 shows reduction profiles of the four supports. Ceria shows the expected H_2 consumption peaks: from ~200-600 ^{0}C and >700 ^{0}C related to surface and bulk reductions of CeO_2, respectively. Upon 10wt.% addition of Sm, Pr and Nd, more intense peaks of reduction are observed between 250-450˚C along with a continuous H_2 consumption section between 600-700˚C possibly indicating a mixed phase reduction.

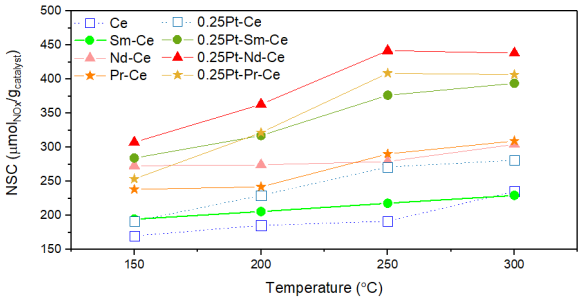

Figure 1. NSC experiments *(Ce = Ceria)

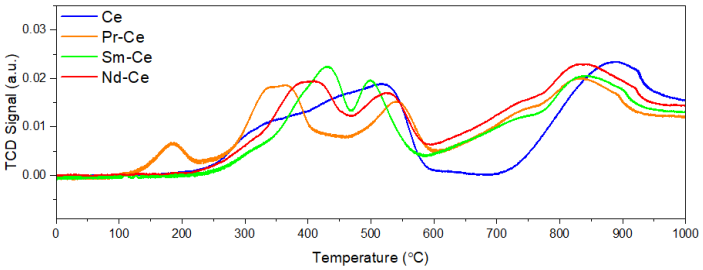

Figure 2. H_2-TPR experiments *(Ce = Ceria)

Many other characterisation techniques have also been used to study catalyst modification with doping. XPS highlighted an increase in surface O content present on the doped samples. Raman spectroscopy investigations showed higher defect densities on doped surface. EELS imaging illustrated partial separation of Pt at the CeO_2 surface caused by Sm doping which affects the Pt-Ce bonding. These studied effects may help explain the greater catalytic performances of the doped catalysts to remove NOx at low temperatures.

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Interaction between Sorbent and Metal Catalyst in a Dual Functional Material for the Direct Air Capture & Conversion of CO_2

Freek Karaçoban, Tomas van Haasterecht, Harry Bitter
Wageningen University, Wageningen, The Netherlands

Keywords: Direct air capture, Carbon dioxide, Dual functional material, Potassium carbonate, Ruthenium

Introduction.

To combat climate change, approaches to capture and convert CO_2 are developed. One of these is dual functional materials (DFMs) that combine a CO_2 sorbent and catalyst. In the presence of H_2, the gaseous or captured form of CO_2 is partially converted. In DFMs, endothermic CO_2 desorption is coupled to exothermic CO_2 hydrogenation, resulting in an integrated heat exchange. Here we will show that sorbent/catalyst interactions exist in a DFM of K_2CO_3 (sorbent) and ruthenium nanoparticles (catalyst) supported on α-Al_2O_3.

$$K_2CO_3 + CO_2 + H_2O \underset{\text{Upon heating, 100-150 °C}}{\overset{\text{Ambient air, room temperature}}{\rightleftharpoons}} 2\ KHCO_3 \xrightarrow[\text{Ruthenium}]{H_2} K_2CO_3 + CH_4 + H_2O$$

Experimental/methodology.

The aim of this study was to identify interactions between K_2CO_3 and Ru in a DFM. To do so, the DFM Ru/K_2CO_3/α-Al_2O_3 was compared to a physical mixture of Ru/α-Al_2O_3 and K_2CO_3/α-Al_2O_3.

To synthesize the DFM, the support was impregnated with ruthenium(III) nitrosyl nitrate. After drying and a heat treatment in N_2 at 450 °C, the support was impregnated with K_2CO_3. The materials were tested in a packed bed reactor through which air (420 ppm CO_2) was flown at 30 °C to capture CO_2. The reactor was then heated to 200 °C (10 °C min^{-1}) under H_2. CO_2 was quantified using an IR detector and hydrogenation products were identified using mass spectrometry.

Results and discussion.

Figure 1A shows the CO_2 concentration and the massspectrometer m/z=15 signal (methane) during the desorption/conversion phase. CO_2 desorbed over a temperature range of 60-150 °C. The physical mixture produced methane over a temperature range of 100-200 °C, while this occurred at a higher temperature for the DMF around 200 °C. We hypothesize that in the DFM, reactive intermediates are more strongly bound to the ruthenium surface, hence methane is released at a higher temperature. In such a material, the conversion should thus be directly correlated with available Ru sites.

To investigate this, the loadings of Ru and K_2CO_3 were varied on the DFM (Figure 1B). By increasing Ru loading from 0.7 to 2.4 wt%, CO_2 conversion increased. An increase in conversion was also achieved by lowering K_2CO_3 loading from 10 to 2.5-5 wt%. The improved conversion with increased Ru loading is likely a result of more available Ru sites. Potentially, K_2CO_3 partially covers the Ru surface with a 10 wt% loading. Lowering the K_2CO_3 loading to 2.5-5 wt% might thus make more sites available, increasing conversion.

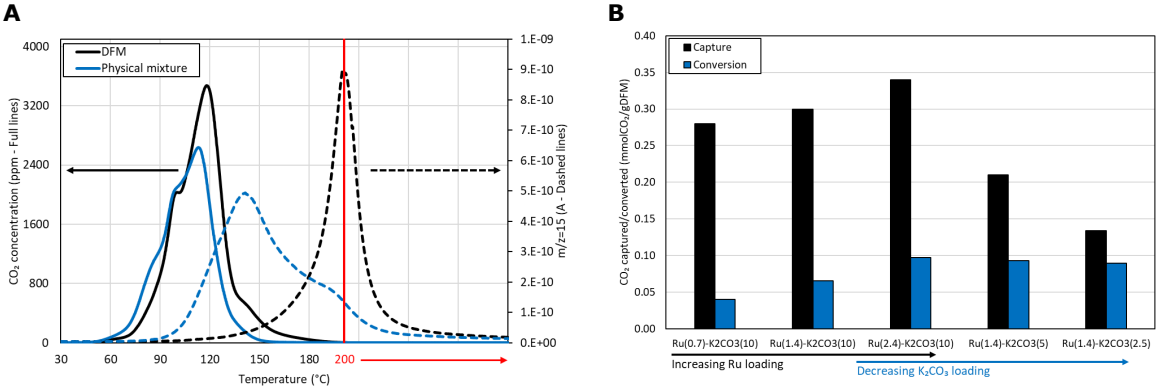

Figure 1: A) CO_2 concentration (full lines) and mass spectrometry m/z=15 signal (dashed lines) during the desorption/conversion phase of the DFM (black) and physical mixture (blue). B) CO_2 capture and conversion for materials with various Ru/K_2CO_3 loadings. Weight loadings (%) in both figures are between brackets.

Mechanism for SO_2 Poisoning of Cu-CHA during Low Temperature NH_3-SCR

J.D. Bjerregaard[1*], M. Votsmeier[2], H. Grönbeck[1]

[1]*Department of Physics, Chalmers University of Technology, Gothenburg, Sweden*
[2]*Umicore AG & Co. KG, Hanau, Germany*
[*]*Joachim.bjerregaard@chalmers.se*

Introduction. Copper exchanged chabazite (Cu-CHA) is state-of-art catalyst for deNOx by ammonia-assisted selective catalytic reduction (NH_3-SCR) in diesel emission control. It is widely used thanks to its good low-temperature activity and hydrothermal stability [1]. However, the catalyst is sensitive to small amounts of sulfur species present in the exhaust stream that accumulate in the catalyst and lead to deactivation over time [2]. A better understanding of the deactivation mechanism is desired to develop catalysts with higher sulfur resistance. The objective of this study is to propose a mechanism for SO_2 poisoning of Cu-CHA during low temperature NH_3-SCR from first principles calculations. This work has been previously published in the Journal of Catalysis, volume 417, January 2023.

Experimental/methodology. Spin polarized density functional theory calculations have been performed in the Vienna Ab initio Simulation Package (VASP). The PBE functional is used to describe the exchange-correlation term, augmented with Grimme 3D approach to describe van der Waals interactions, and a Hubbard term to describe the localization of electrons in the 3d orbital of Cu. Transition states are located using climbing image nudged elastic band (CI-NEB) and ab initio molecular dynamics (AIMD) simulations are performed to investigate the flat energy landscape and to study diffusion of Cu species. Ab initio thermodynamic analyses are carried out to study the stable structures at reaction conditions.

Results and discussion. During typical reaction conditions, the Cu ions are solvated by NH_3, forming $[Cu(NH_3)_2]^+$ [3], which are inter-cage mobile. If two $[Cu(NH_3)_2]^+$ complexes are present in the same cage, O_2 can be activated, forming $[Cu_2(NH_3)_4O_2]^{2+}$, which is a critical step in low-temperature NH_3-SCR [4]. We find that SO_2 forms a stable complex $[Cu_2(NH_3)_4SO_4]^{2+}$ when interacting with $[Cu_2(NH_3)_4O_2]^{2+}$. We propose a reaction mechanism in which NH_3 and NO couple over $[Cu_2(NH_3)_4SO_4]^{2+}$ forming H_2SO_4, H_2O and N_2. The inter-cage diffusion of H_2SO_4 has a barrier of 1.45 eV suggesting that sulfur might accumulate inside the CHA-cage. Furthermore, we find that H_2SO_4 can undergo an acid-base reaction and that $HSO_4(NH_4)$ is most stable species at typical reaction conditions. Based on these results, we investigate how the presence of multiple $HSO_4(NH_4)$ species in the CHA-cage may deactivate the catalyst. Constrained AIMD simulations are performed to investigate the stability of paired $[Cu(NH_3)_2]^+$ complexes in presence of zero, one or two $HSO_4(NH_4)$ species, and results are shown in Figure 1. We conclude that the pairing of $[Cu(NH_3)_2]^+$ is destabilized in presence of two $HSO_4(NH_4)$ species, which prevents O_2 activations. This gives a possible explanation for how $HSO_4(NH_4)$ deactivates the catalyst. Our results suggest that low-temperature SO_2 poisoning is of physical character, in which the presence of sulfur species hinders the activation of O_2 over two $[Cu(NH_3)_2]^+$ complexes. Thus maintaining facile diffusion of $[Cu(NH_3)_2]^+$ is critical for preventing loss in SCR activity.

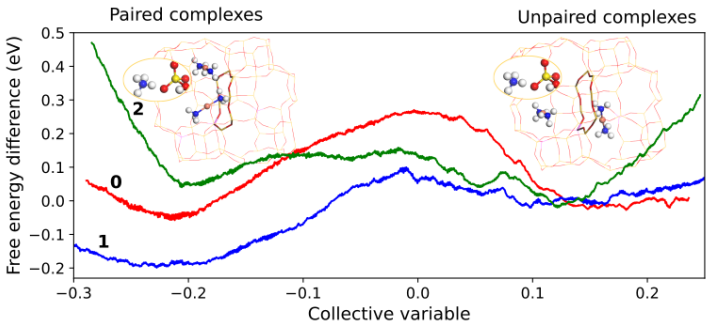

Figure SEQ Figure * ARABIC 1 - AIMD simulations for diffusion of a [Cu(NH3)2]+ complex through an eight-membered ring in presence of zero (red), one(blue) and two (green) HSO4(NH4) in the cage.

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Structural characteristics leading to a high CH_4 oxidation activity for Pd/CeO_2-based catalysts

D. Zengel[1], F. Maurer[1], A. Salcedo[2], C. Michel[2], D. Loffreda[2], M. Aouine[3], T. Epicier[3], S. Loridant[3], P. Vernoux[3], M. Casapu[1*], J.-D. Grunwaldt[1]

[1]*Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*

[2]*ENS de Lyon, CNRS UMR 5182, Laboratoire de Chimie, Lyon, France*

[3]*Institut de Recherches sur la Catalyse et l'Environnement de Lyon, CNRS UMR5256, Université de Lyon, Lyon, France*

[*]*maria.casapu@kit.edu*

Keywords: methane oxidation, noble metal clusters, emission control

Introduction. Methane/biomethane is a key energy carrier for the transition from fossil to more sustainable resources. Due to the high hydrogen-to-carbon-ratio in CH_4, the CO_2 emissions can be significantly reduced compared to those resulting from the combustion of other hydrocarbons [1], with a major decrease recorded especially for biomethane and methane obtained from green hydrogen. Nevertheless, an important drawback is the high greenhouse gas potential of methane itself. Among different catalysts tested for reducing the CH_4 slip, Pd-based systems are known to show the highest efficiency. However, they still suffer from sulfur poisoning and water deactivation. Numerous attempts have been undertaken to understand the deactivation and regeneration behavior of Pd-catalysts, and a clear influence of the carrier material and gas composition was observed [2,3].

Experimental/methodology. A series of Pd-CeO_2 based catalysts with different noble metal loadings (13 wt.%) were prepared by incipient wetness impregnation. After different pre-treatment procedures, the catalytic performance was investigated in plug-flow reactor between 200-550 °C using a gas mixture containing 3200 ppm CH_4, 10% O_2 in N_2. To obtain structure-activity correlations, the catalysts were characterized by complementary *in situ* and *ex situ* methods including: X-ray diffraction (XRD), temperature programmed reduction, electron microscopy and X-ray absorption spectroscopy (XAS). Additionally, the nature of active species was identified by *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements supplemented by density functional theory (DFT) calculations.

Results and discussion. The results obtained in this study indicate a strong impact of catalyst pre-treatment conditions on the activity of Pd/CeO_2-catalysts. Whereas an oxidizing treatment at high temperatures results in catalyst deactivation, a significant activity gain was obtained upon reduction in CO- or H_2-containing gas mixtures. In line with our previous studies [4,5], this positive effect of a reducing treatment could be correlated with the tuning of the interface between the reduced noble metal nanoparticles and ceria support. The formation or redispersion of Pd nanoparticles depending on the catalyst treatment was revealed by environmental transmission electron microscopy (ETEM) measurements. Further differences in the noble metal structure leading to a higher or lower catalyst durability were uncovered by *in situ* DRIFTS and *operando* XAS characterization, and were additionally supported by DFT calculations [6].

Acknowledgments

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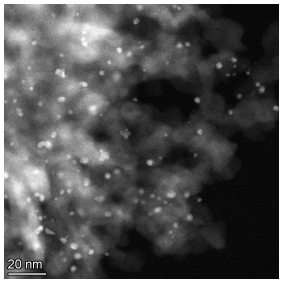
Influence of the preparation method on structure, activity and stability of bimetallic $PtPd/Al_2O_3$ catalysts for emission control

J. Czechowsky[1*], P. Dolcet[1], C. B. Maliakkal[2], M. Crone[3], R. Popescu[4], H. Störmer[4], S. Gross[5], S. Behrens[6], M. Türk[3], J.-D. Grunwaldt[1, 6], M. Casapu[1*]

[1]*Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology, Karlsruhe, Germany*
[2]*Institute of Nanotechnology (INT), Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany*
[3]*Institute for Technical Thermodynamic and Refrigeration (ITTK), Karlsruhe Institute of Technology, Karlsruhe, Germany*
[4]*Laboratory for Electron Microscopy (LEM), Karlsruhe Institute of Technology, Karlsruhe, Germany*
[5]*Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Padova, Italy*
[6]*Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany*
[*]*joachim.czechowsky@kit.edu; maria.casapu@kit.edu*

Introduction. Pt and Pd are commonly used in emission control for catalytic oxidation of harmful and toxic pollutants such as carbon monoxide, nitrogen oxide or hydrocarbons. Their limited supply, however, requires an efficient use. One option to increase the activity, stability and poisoning tolerance of such catalysts is the use of bimetallic PtPd samples. [1] Despite numerous studies have reported synergistic effects, the exact nature of Pt-Pd interaction, noble metal distribution and state as well as the surface/bulk composition of bimetallic particles are still subject to extensive discussion. [2, 3, 4] In our study, the impact of the catalyst preparation method on the Pt-Pd bimetallic particle structure and evolution during CO, NO and CO/NO oxidation is systematically investigated.

Experimental/methodology. Catalysts containing 1 wt% Pt and 1 wt% Pd on γ-Al_2O_3 were prepared by conventional and advanced preparation methods such as incipient wetness impregnation, colloidal synthesis, supercritical fluid reactive deposition and flame spray pyrolysis. [4, 5, 6] The resulting samples were in-depth characterized by XRD, TEM, EDXS, N_2-physisorption and *in situ* XAS measurements. Activity tests were conducted for CO-, NO- and combined CO/NO-oxidation in excess oxygen.

(a) 

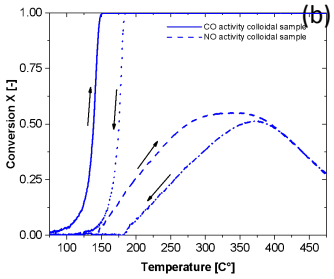
(b) 

Fig.1: (a) Uniform distribution of PtPd particles obtained by colloidal synthesis on γ-Al_2O_3 support; (b) Corresponding CO and NO oxidation activity

Results and discussion. Significant differences in Pt-Pd nanoparticle size, structure and composition were obtained by varying the preparation procedure. In general, a poor catalyst uniformity was found for most conventional synthesis methods. In contrast, a high alloying degree and good distribution resulted by colloidal synthesis of bimetallic nanoparticles. Such uniform Pt-Pd bimetallic catalysts allow a better understanding of the CO, NO and CO/NO conversion profiles in comparison to those obtained for the corresponding Pt and Pd-monometallic samples. Combined with *ex situ* and *in situ* characterization, the emerging characteristics of this class of bimetallic catalysts and their advantages as well as functionality can be unambiguously identified.

Acknowledgments
This work was supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) Project ID426888090-SFB 1441 ("TrackAct") Project B2.

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In-situ investigation of the Pd-Ce interaction evolution under stoichiometric CH_4 oxidation conditions

Maila Danielis[1], Núria J. Divins[2,3], Jordi Llorca[2,3], Lluís Soler[2,3], Xènia Garcia[2,3], Isabel Serrano[3], Luis E. Betancourt[4], Wenqian Xu[5], José A. Rodríguez[4], Sanjaya D. Senanayake[4], Sara Colussi[1] and Alessandro Trovarelli[1*]

[1]Polytechnic Department, University of Udine, and INSTM, 33100 Udine, Italy; [2]Institute of Energy Technologies and Department of Chemical Engineering, Universitat Politècnica de Catalunya, EEBE, 08019 Barcelona, Spain; [3]Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, EEBE, 08019 Barcelona, Spain; [4]Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973, USA; [5]X-ray Science Division, APS, Argonne National Laboratory, Lemont, IL, 60439 USA
[*]alessandro.trovarelli@uniud.it

Introduction. The oxidation of CH_4 under stoichiometric feed represents a key point for the performance of Pd-based Three Way Catalysts (TWC) for Natural Gas fueled Vehicles (NGVs) [1]. The absence of excess O_2 leads to facile reduction of PdO to metallic Pd^0 species, which are only active on pure Al_2O_3 if high dispersion is maintained [2]. Other studies report that balanced core-shell Pd-PdO particles possess high activity, but rich-lean pulses are required, leading to a sensible increase in fuel consumption [3]. Here, we study the evolution of Pd-CeO_2 catalysts prepared by dry milling under stoichiometric conditions [4] prompted by the unique behavior displayed under lean and rich methane abatement conditions [5,6].

Experimental. 4wt%Pd/CeO_2 catalysts were prepared by milling (M) and by incipient wetness impregnation (IW) following established procedures [4,5] on commercial ceria (BET S.A.≈25 m^2g^{-1}). CH_4 oxidation tests were carried out on 30 mg of powder sample at a GHSV=400000 h^{-1} under dry (0.5% CH_4, 1% O_2 in He) and wet (with 10vol% H_2O) gas feed conditions. The Pd and CeO_2 surface and bulk structure were followed *in-situ* by synchrotron X-ray Diffraction (XRD) and Ambient-Pressure X-ray Photoelecton Spectroscopy (XPS).

Results and discussion. Under stoichiometric 1:2 CH_4:O_2 feed the samples prepared by milling (M) outperformed the reference IW catalyst, with a measured reaction rate of 13.5 *vs* 4.8 $\mu mol_{CH4} \cdot g_{Pd}^{-1} \cdot s^{-1}$, respectively, in dry conditions at 563K, and 14.9 *vs* 4.2 $\mu mol_{CH4} \cdot g_{Pd}^{-1} \cdot s^{-1}$ at 613K in wet conditions. *In-situ* XRD analysis revealed stable particle size during reaction, likely due to the high temperatures reached during a pre-treatment oxidation cycle (1173K) to simulate real catalyst operation. Remarkably, the main differences are observed by AP-XPS spectra (Figure 1), which highlight a balanced Pd:PdO ratio on the Milled sample and predominant Pd^{2+} on the IW sample. In addition, heavy accumulation of OH species on the IW catalyst is observed, indicating it as the main inhibition mechanism on the standard catalyst. The reported results show the unique role of CeO_2 as a support oxide, promoting the generation of a mixed Pd^0/Pd^{2+} state which appears to be the best performing state in interaction with CeO_2, compared to pure Pd^0 on Al_2O_3 [2] or predominant Pd^{2+} under lean conditions [5,6].

Figure 1. NAP-XPS spectra collected in the Pd 3d (A,C) and O 1s (B,D) regions under 0.6 mbar CH_4, 1.4 mbar O_2 at increasing temperatures (673K, 773K, 873K). (A-B): 4PdCeIW, (C,D): 4PdAcCeM.

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Non-stoichiometric spinels ferrites ($Co_xFe_{3-x}O_4$ and $Mn_xFe_{3-x}O_4$) in study on methane oxidation

A. DECOSTER*, F. DHAINAUT, P. GRANGER

Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de catalyse et Chimie du solide, F-59000 Lille, France

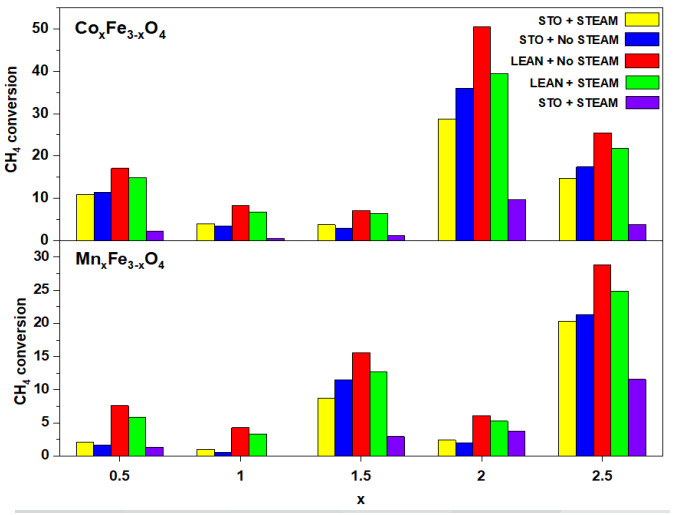
*Corresponding author: Email: amaury.decoster.etu@univ-lille.fr

Keywords: Methane oxidation, induction heating, spinel ferrite

Introduction: Natural gas vehicles (NGV) are an alternative solution to fossil fuelled engines to reduce CO_2 emissions and lower the contribution to the greenhouse gas effect. The abatement of low unburnt methane emissions from the exhaust is a prerequisite due to methane's greenhouse gas effect higher than CO_2. [1][2] Pd-catalysts are recognized as benchmark for this application mostly in lean conditions. Presently, the development of platinum group metal free catalysts is strongly encouraged capable to run in more representative three-way operating conditions, e.g. near stoichiometry. The catalytic performances of novel spinel $Co_xFe_{3-x}O_4$ and $Mn_xFe_{3-x}O_4$ catalysts have been evaluated in terms of activity and thermal stability. In parallel their magnetic properties were studied in order to set up induction heating technology with the aim to enhance catalysis and lower the operating temperature conditions.

Experimental/methodology: $M_xFe_{3-x}O_4$ catalysts were prepared according to a conventionnel precipitation method. Structural analyses were made by XRD and Raman. Determination of oxidation states was made by XPS. Reducibility behaviours were studied by H_2-TPR analysis and cation distribution was done by Mössbauer spectrometry. Moreover, Vibrating Sample Magnetometer (VSM) was used to determine magnetic behaviour of all spinels and conclude on heating mechanism. Catalytic performed at 600°C in a plug flow reactor (figure 1) in stoichiometric and lean condition in the presence and in the absence of steam.

Results and discussion: XRD and Raman analyses confirmed predominant spinel structure but showed a structural modification which induce by change in the reducibility. Mössbauer spectra of $Co_xFe_{3-x}O_4$ provide additional information related to the migration of Co inside the lattice. Ferromagnetic behaviour was characterized at 2K while paramagnetic and superparamagnetic behaviours prevail at high temperature. These magnetic features underline the fact of no hysteresis heating can be done at room temperature for all spinels. Steady-state rate measurements reveal that Co_2FeO_4 exhibits the best activity. On the other hand, improved thermal stability was observed on the serie $Mn_xFe_{3-x}O_4$ with acceptable conversions. We observe globally a negative impact of steam and positive order with respect to oxygen concentration.



Acknowledgments:
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Cu-doped cryptomelane and spinel $Cu_xMn_{3-x}O_4$ catalysts for CO oxidation

H. Pan[a,b,1], X. Chen[a,1,e,*], C. López-Cartes[c], J. Martínez-López[d], E. Bu[a, e],

J.M. Rodríguez-Izquierdo[a, e], J.J. Delgado[a, e,*]

[a] *Departamento de Ciencia de los Materiales, Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz, Campus Río San Pedro, Puerto Real (Cádiz), E-11510, Spain*

[b] *Henan Key Laboratory of Industrial Microbial Resources and Fermentation Technology, College of Biological and Chemical Engineering, Nanyang Institute of Technology, Nanyang 473004, PR China*

[c] *Inorganic Chemistry Department, Faculty of Chemistry, University of Seville, Seville, Spain*

[d] *Departamento de Ciencias de la Tierra, Universidad de Cádiz, Campus Río San Pedro, Puerto Real (Cádiz).*

[e] *Instituto Universitario de Investigación en Microscopía Electrónica y Materiales (IMEYMAT), Universidad de Cádiz, Campus Río San Pedro, Puerto Real (Cádiz), E-11510, Spain*

Keywords: Cryptomelane, $Cu_{1.5}Mn_{1.5}O_4$ spinel, CO oxidation, redox property

Introduction: Carbon monoxide (CO) removal is one of the most studied reaction in catalysis due to the high toxicity of this gas and because it is accepted as a model reaction [1]. Some of the commercially available catalyst are based on $CuMn_2O_4$ spinel and their activity is normally attributed to the flexibility of the Cu^+/Cu^{2+} and Mn^{3+}/Mn^{4+} couples, which improve their redox properties and activate the CO molecule [2].

Experimental/methodology. A series of Cu-MnOx catalysts were synthesized by a hydrothermal method using an aqueous solution of $KMnO_4$ and $Cu(NO_3)_2$ and ethanol as the reducing agent. The autoclave was heated to 100°C for 12 hours. The samples were dried overnight and then calcined at 500°C for 6 hours. The catalytic tests were performed using 50 mg of catalyst diluted with 100 mg of SiC, with a total flow rate of 100 mL/min and a gas composition of 1 vol.% CO, 0.6 vol.% O2, and 98.4 vol.%.

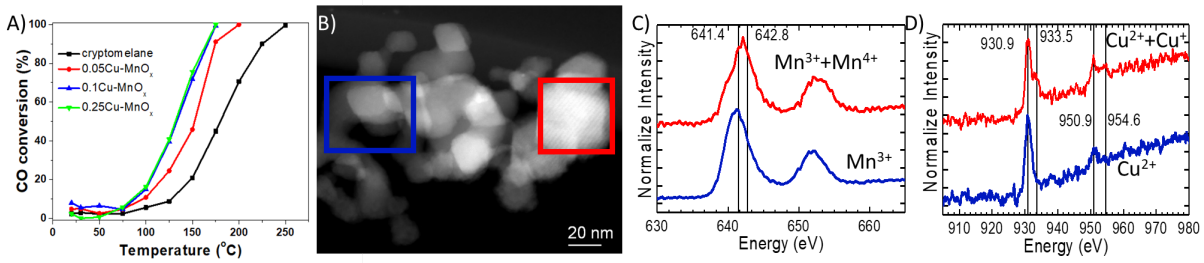

Figure 1 Catalytic performance of the samples (A), HAADF image where the EELS experiment were performed (B), Mn-$L_{2,3}$ edge(C) and Cu-$L_{2,3}$ (D) of the marked areas.

Results and discussion.

All catalysts were profoundly characterized using XRD, XRF, N_2 physisorption, XPS, TPD, CO-TPR and advanced transmission electron microscopy techniques (HAADF-STEM, EELS and EDS). The results revealed that the Cu:Mn molar ratio of the precursors had a significant impact on the crystalline structure and morphology of the synthesized samples. A Cu-doped cryptomelane with a nanorod morphology was observed when the Cu:Mn molar ratio was 0.05. Conversely, different mixture of Cu-doped cryptomelane nanorods, Mn_2O_3, and $Cu_{1.5}Mn_{1.5}O_4$ spinel nanoparticles were formed at higher molar ratios. As shown in Figure 1, the addition of Cu improves the catalytic activity and the presence of the Mn and Cu with different oxidation states was proven by EELS experiments. The effect of the redox properties and the coexistence of the manganese and copper with different oxidation states will be discussed.

Acknowledgments

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Ceria and praseodymia-based catalysts for the removal of gaseous pollutants from oxyfuel engines

A. Díaz-Verde[1*], J. C. Martínez-Munuera[1], A. García-García[1], P. Piqueras[2], E. J. Sanchis[2]

[1]*Carbon Materials and Environment Research Group. Inorganic Chemistry Department and Institute of Materials. University of Alicante. Alicante. Spain.*
[2]*Universitat Politècnica de València, CMT-Motores Térmicos. Valencia. Spain.*
[*]*alvaro.diaz@ua.es*

Keywords: ceria, praseodymia, copper, OSC, CO oxidation.

Introduction.

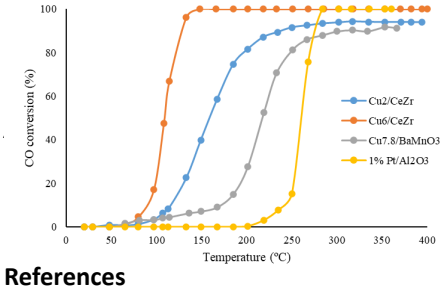
Nowadays, there is an important need to decrease global greenhouse gas emissions from vehicles exhaust. For this reason, ambitious measures must be taken in the automotive sector concerning improvements in engine combustion. In this sense, oxyfuel engines, capable of capturing the CO_2 emitted that can be used, eventually, for e-fuels processing, seems to be a promising option. To reach adequate aftertreatment systems, new catalytic formulations should be proposed under these demanding conditions. In this line, a catalytic system based on two phases should be designed: i) one of them able to capture and supply oxygen (e.g. ceria-praseodymia based oxides) in stoichiometric combustion engines, and ii) other one to promote the CO oxidation (e.g. copper/ceria-zirconia based catalysts) in lean combustion engines.

Experimental/methodology.

$Ce_{0.3}Pr_{0.7}O_2$ catalyst (CePr) has been synthesized by the direct calcination method of the metallic precursors [1]. Several conditions to evaluate its capacity to capture and release oxygen have been tested (Fig. 1). On the other hand, $Ce_{0.8}Zr_{0.2}O_2$ (CeZr) formulation has been synthesized using the co-precipitation method, and two copper loadings (2 and 6 %, respectively) have been introduced by the incipient wetness impregnation procedure. CO oxidation experiments were performed under Temperature-Programmed Reaction conditions using several reactant mixtures typical of conventional and oxy-fuel combustion exhausts.

Results and discussion.

Experiments of oxygen capture and subsequent release revealed that CePr catalyst could capture and emit oxygen between the 25 and 40 % of the total available oxygen with respect to that which would be released under reducing conditions, and the amount and rate of the oxygen release depend on the heating rate used, as reflected on Fig.1 (left). On the other hand, CO oxidation tests showed that Cu/CeZr catalysts present a better catalytic performance under oxy-fuel conditions than under conventional ones, and higher copper loadings allow increasing CO conversion efficiency, (see Fig. 1 (right)), and promote resistance to inhibition due to CO_2 presence, exhibiting much better performance than a commercial 1% Pt/Al_2O_3 and a home-made perovskite ($Cu7.8/BaMnO_3$).



t atmosphere of CePr (left) and CO conversion profiles of Cu/CeZr catalysts % O_2 + 1.9 % CO reactant mixture (right).

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CO oxidation performance in GDI engine exhaust conditions of $Ba_xMn_{0.7}Cu_{0.3}O_3$ (x = 1, 0.9, 0.8 and 0.7) perovskite catalysts

A. Díaz-Verde[1*], E. L. dos Santos Veiga[2], H. Beltrán-Mir[2], V. Torregrosa-Rivero[1], M. J. Illán-Gómez[1], E. Cordoncillo-Cordoncillo[2]

[1]*Carbon Materials and Environment Research Group. Inorganic Chemistry Department. University of Alicante. Alicante. Spain.*
[2]*Inorganic and Organic Chemistry Department. University Jaume I. Castellón de la Plana. Spain.*
[*]*alvaro.diaz@ua.es*

Keywords: perovskite, barium, manganese, CO oxidation, GDI engines.

Introduction.

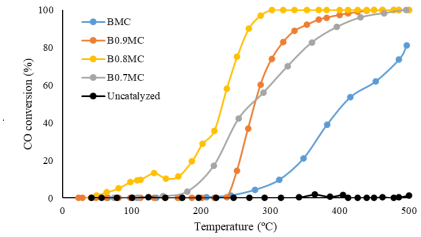
Mixed oxides with perovskite-type structure (ABO_3) [1] present interesting catalytic properties to be used for atmospheric pollution control, being a promising alternative to noble metal based catalysts. A series of $BaMn_{1-x}Cu_xO_3$ perovskites has been studied for diesel soot oxidation, being $BaMn_{0.7}Cu_{0.3}O_3$ the best catalyst for this reaction. Additionally, the high selectivity to CO_2 observed for this catalyst revealed its high capacity to oxidise CO to CO_2 [2]. Therefore, in order to improve the catalytic performance for CO oxidation, in this work a series of $Ba_xMn_{0.7}Cu_{0.3}O_3$ (x = 1, 0.9, 0.8 and 0.7; named as BxMC) has been synthesized, characterized and tested for this reaction carried out in GDI engine exhaust conditions.

Experimental/methodology.

The synthesis of perovskite type catalysts was carried by the sol-gel method adapted to aqueous medium [2]. The catalysts were characterized by XRD, ICP-OES, H_2-TPR, XPS, impedance spectroscopy and O_2-TPD techniques. Catalytic activity for CO oxidation has been studied in Temperature-Programmed Reaction conditions (TPR) using three reactant mixtures: i) 0.1% CO + 1%O_2; ii) 1% CO + 1% O_2; and iii) 1% CO + 10% O_2. Stability and reciclability tests have also been performed for the most active samples.

Results and discussion.

XRD results showed that, as Ba content decreases, a change from h-polytype structure (a distortion of the hexagonal perovskite structure caused by the insertion of copper into the network of perovskite [1]) to hexagonal perovskite structure is promoted. H_2-TPR results reveal a Mn-Cu synergetic effect which allows a decrease in the temperature for Mn(IV)/Mn(III) reduction to Mn(II) and, finally, XPS results revealed the presence of surface oxygen vacancies. In Figure 1 the CO conversion profiles versus temperature for 1% CO + 1% O_2 reactant mixture is featured. All catalysts tested are active for CO oxidation, being the activity related with the amount of oxygen vacancies and copper located on the surface of catalysts.



ı profiles for $Ba_xMn_{0.7}Cu_{0.3}O_3$ in 1% CO+1% O_2 reactant mixture.

ʳt to Spanish Government (MINCINN:Proyect PID2019-105542RB-I00), European ıciana (Proyect CIPROM/2021-070).

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Exploiting Proximity Effects of highly dispersed Pt Species on CeO_2 for Improved Emission Control

F. Maurer[1], P. Dolcet[1], A. Beck[1], J. Jelic[2], F. Studt[2], M. Casapu[1], J.-D. Grunwaldt[1*]

[1]Instituite for Chemical Technology and Polymer Chemistry, *Karlsruhe Institute of Technology, Karlsruhe, Germany;* [2]Institute of Catalysis Research and Technology, *Karlsruhe Institute of Technology, Karlsruhe, Germany; *grunwaldt@kit.edu*

Introduction.

Catalysts based on supported noble metal (NM) particles play an important role in the synthesis of fine chemicals, fuel cells and also for the removal of environmentally harmful and toxic emissions. Due to their scarcity and costs, an efficient usage of these metals is therefore highly desirable. In this regard, the NM-support interaction, particularly for platinum group metals supported on CeO_2, gained strong attention. Particularly, this interaction leads to Pt redispersion under oxidizing conditions, enabling regeneration strategies for sintering.[1] Also, in the CO oxidation reaction, which is a model reaction for clean air emission control, Pt particles in the presence of CeO_2 were shown to be less inhibited by CO poisoning. The combination of both properties of Pt/CeO_2 gives an interesting opportunity to tune and exploit the interaction with the support. In this study, we investigate highly dispersed Pt species with maximized NM-support interface on CeO_2 to identify the active Pt species[2] and to improve the catalyst design by tuning the surface noble metal concentration[3].

Experimental/methodology.

Pt/CeO_2 based catalysts with varying Pt loadings (1.0 wt %, 2.3 wt % and 4.5 wt %) were synthesized by incipient wetness impregnation. As support, hydrothermally (100 °C for 21 h) prepared CeO_2 nanorods from $Ce(NO_3)_3 \cdot 6\ H_2O$ were used.[3] The CO oxidation activity were performed in plug-flow geometry. The catalyst, the mass of which was adjusted to the Pt loading, was used as sieved fraction and was diluted by SiO_2 (grain size of 125–250 µm) to a total of 1 g. In this way, a constant weight hourly space velocity (WHSV) of 60 000 L g_{Pt}^{-1} h^{-1} was retained for all samples. *In situ* and *operando* X-ray absorption spectroscopic (XAS) measurements at the Pt L_3 edge were performed at the CATACT and XAS beamlines of the KIT Light source and at P65 at DESY using a fluorescence detector.[2,3] For all experiments a quartz micro reactor (1-2 mm diameter) was filled with 7-10 mg of undiluted catalyst.

Results and discussion.

The initial state of Pt in all 3 catalyst samples was investigated by means of Transmission Electron Microscopy (TEM) and extended X-ray absorption fine structure spectroscopy (EXAFS). In all cases, Pt was found to be highly dispersed and oxidized. EXAFS fitting indicated the presence of both, single atomic species[2] and clusters.[3] Depending on the Pt weight loading, and thus surface noble metal concentration (SNMC), the samples varied strongly in CO oxidation activity. The ignition temperature of CO oxidation decreased by ~200 °C when going from the sample with the lowest SNMC to the one with the highest SNMC. This behaviour could be related to the Pt cluster formation by further Raman, *in situ* infrared and *operando* X-ray absorption spectroscopic investigations.[3] Together with DFT calculations, we were able to show that at a higher SNMC the Pt agglomeration is favoured statistically due to the proximity of Pt atoms, which is also lowering the Pt diffusion barriers on the CeO_2 surface. Our study emphasizes how the dynamics of Pt can be used to increase and stabilize the low temperature activity of such catalysts.

Acknowledgments

The authors gratefully acknowledge the German Research Foundation (DFG) for the financial support of the SFB 1441−Project-ID 426888090.

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Preparation of High Performance CeO_2-ZrO_2 for Automotive OSC Material and its Surface Analyses

M. Inoue[1], S. Watanabe[1], M. Yamaguchi[1], T. Osako[1], K. Kato[1], Y. Kobayashi[1], Y. Nagao[1], Y. Endo[1*], T. Wakabayashi[1], M. Haneda[2]

[1]*Mitsui Mining & Smelting Co., Ltd., Ageo, Japan*
[2]*Nagoya Institute of Technology, Advanced Ceramics Research Center, Tajimi, Japan*
[*]*Corresponding Author: yo_endo@mitsui-kinzoku.com*

Keywords: CeO_2-ZrO_2, OSC material, Three-way catalyst, Automotive catalyst, Gasoline exhaust

Introduction. For stringent regulations of exhaust gasses from gasoline-powered vehicles, highly active three-way catalysts (TWCs) even at low temperature are strongly required [1]. Improvement of oxygen storage capacity (OSC) at low temperature is the most effective way to satisfy this requirement. In this study, we have developed low temperature active CeO_2-ZrO_2 material (CZ) based on new synthetic procedure and surface analysis.

Experimental. SCW-CZ shown below was prepared by the procedures as follows. A solution of $ZrO(NO_3)_2$ (162.3 mmol), $Ce(NO_3)_3$ (93.0 mmol), $La(NO_3)_3$ (4.91 mmol), $Nd(NO_3)_3$ (9.51 mmol), and $Pr(NO_3)_3$ (9.40 mmol) in H_2O (370 mL) was added slowly-dropwise to an aqueous NH_3 (11wt%, 200 g) while taking a time of 80 minutes to neutralize the reaction mixture. The resulting precipitation was filtered, washed, and re-added to H_2O to give a slurry (3.3 wt%). The slurry was treated under supercritical/subcritical condition (350 °C, 25MPa) using high pressure reactor. Following that, the treated slurry was dried at 120 °C overnight. The titel compound was given as beige colored complex oxide.

Results and discussion. In general, OSC of CZ is strongly affected by homogeneity of Ce and Zr conformation in the crystal structure. Homogeneous CZ as solid solution is equivalent to highly-crystallized CZ prepared by high temperature calcination (HTC) around at 1000 °C. However, HTC usually causes growth of crystal diameter and low surface area, which directly leads to decreasing OSC performances at low temperature [2]. Treatment with supercritical/subcritical water (SCW) is significant procedure to obtain homogeneous CZ without any HTC. It also makes a strong effect on diffusion behavior during formation of oxide precursor, resulting in unique distribution of Ce/Zr cations on the surface. To understand the details of CZ surface, CH_3OH adsorption following IR spectroscopy can be often used [3]. Its spectrum provides the states of coordinatively saturation around Ce and Zr atoms involving the homogeneity. Figure 1 exhibits that SCW-CZ and HTC-CZ have larger ratio of peak area at 1035 cm^{-1} and 1077 cm^{-1} based on the area at 1105 cm^{-1} than the conventional CZ (C-CZ). In particular, the peaks at 1035 cm^{-1} and 1077 cm^{-1} are attributed to CH_3OH coordination on unsaturated Ce site which could be generated by site replacement of Zr with Ce as well as related to OSC performance. On the other hand, the peak at 1105 cm^{-1} is attributed to saturated Ce site which could not be effective on OSC performance. Subsequently, OSC evaluations were performed at 300 °C and 400 °C. The result shows that SCW-CZ has higher OSC than HTC-CZ even though these CZ have similar surface state. This is because SCW-CZ has much smaller crystal diameter and higher surface area than HTC-CZ shown in Table 2. In conclusion, we found that SCW condition strongly prompts metal-site replacement to give highly-homogeneous CZ having small crystal diameter and high surface area. Accordingly, the obtained SCW-CZ exhibits higher OSC than the others at 300 °C where TWC is not fully-activated.

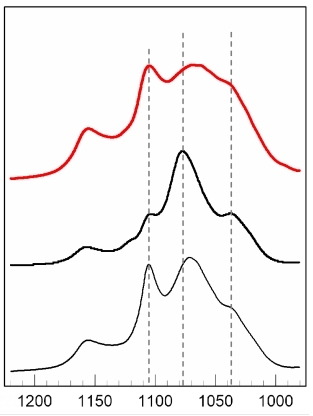

Figure SEQ Figure * ARABIC 1. CH_3OH adsorbed IR spectra.

Table SEQ Figure * ARABIC 2. OSC, XRD, and BET analyses.

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Fe AND Mn PHASES DEPOSITED ON CERIA BIOMORPHIC FIBERS BY GLIDARC PLASMA

M. Rodriguez* [1,2], V.G. Milt [2], E.E. Miró [2], E.M Gaigneaux [1]

[1] *Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Louvain-la-Neuve, Belgium.*
[2] *Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (UNL-CONICET), Santa Fe, Argentina.*
[*] *maximiliano.rodriguez@uclouvain.be*

Introduction: Plasma, known as the fourth state of matter, consists of an ionized gas with unique properties that permit significant improvement of traditional chemical processes, increase their efficiency, and stimulate chemical reactions impossible by conventional methods[1]. When plasma glidarc is used with humid air as feeding gas, some very reactive species are generated, which can carry out oxidation and reduction reactions depending on the target molecules present[2,3]. The oxidative and reductive abilities of glidarc plasma in humid air makes it a very attractive technique for synthesis of metal oxides for heterogeneous catalysis.

Experimental: A batch configuration of glidarc plasma was adopted with humid water as feeding gas[2]. The targets exposed were precursor solutions alone made of potassium permanganate ($KMnO_4$) or ammonium iron (II) sulfate hexahydrate (AFeS). Biomorphic ceria fibers were added in the reactor along with the solution of precursors, expecting the precipitates to anchor or nucleate on their surface. The added fibers (Fib Ce) were synthesized by means of a biotemplate (cotton) which was impregnated with a cerium precursor solution until saturation, then dried and finally calcined to remove the template[4]. The activity of the impregnated fibers for diesel soot oxidation was examined by Temperature programmed oxidation (TPO)[5] using a model soot (Printex U).

Results and discussion: The precipitates obtained after exposing the precursor solutions to glidarc plasma were identified by XRD analysis. A birnessite-type (KMO) and cryptomelane (OMS) phases were obtained after calcination of $KMnO_4$ precipitate at 400 °C and 600 °C, respectively. For AFeS, α-Fe_2O_3 hematite was formed after calcination at 600 °C. After the deposition of Mn in the presence of Fib Ce, no signals were detected beside the ones coming from the support (cubic ceria fluorite). In turn, a characteristic peak of α-Fe_2O_3 was seen for the deposition with AFeS on Fib Ce. Since XRD did not allow us to detect the presence of Mn species, EDX analysis were carried out and the atomic ratios of Mn and Fe referred to cerium were calculated (Table 1). Additionally, XPS quantification analysis confirmed the superficial enrichment of these species on the fibers. As Table 1 shows, the impregnation of Mn (Fib Ce-OMS) enhanced the activity of the bare fibers, whereas the deposition of Fe (Fib Ce-Fe_2O_3) was detrimental, despite being lower the metal content of the former, which highlights the beneficial effect of Mn(IV)-Mn(III) redox couple.

Table 1 - Atomic ratios of plasma-impregnated fibers and T_M values in soot combustion.

Catalyst	EDX*		XPS		T_M (°C)**
	$(Fe/Ce)_{at.}$	$(Mn/Ce)_{at.}$	$(Fe/Ce)_{at.}$	$(Mn/Ce)_{at.}$	
Fib Ce	-	-	-	-	420
Fib Ce - Fe_2O_3	0.18	-	2.47	-	460
Fib Ce - OMS	-	0.06	-	0.32	400

*** Average ratio values calculated from three different mapping zones. ** Temperature at which soot combustion rate is maximum.**

Acknowledgments

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An isotopic study on oxygen interaction and GDI soot combustion over ceria-praseodymia mixed oxides with pulse experiments using $^{18}O_2$

J.C Martínez Munuera[1], M. Cortés Reyes[2], A. García García[1*]

[1]*Grupo MCMA, Departamento de Química Inorgánica e Instituto Universitario de Materiales, Universidad de Alicante, Sant Vicent del Raspeig, Alicante, SPAIN*

[2]*Departamento de Ingeniería Química, Facultad de Ciencias, Campus de Teatinos, Universidad de Málaga, Málaga, SPAIN*

[*]a.garcia@ua.es

Introduction. Due to their improved fuel efficiency, an increase in European and US market penetration is expected for Gasoline Direct Injection (GDI) vehicles in a near future. However, the use of GDI engines also carries unintended consequences, including significantly higher particulate emissions when compared to port-fuel injection (PFI) engines. A first approach to tackle these soot emissions is to incorporate a Gasoline Particulate Filter (GPF) downstream the TWC in the exhaust. However, to avoid severe problems such as growing back pressure due to soot deposition onto the filter, this device should be periodically regenerated. Unfortunately, the typical conditions of the exhaust are very unfavourable for soot combustion. In this demanding context, catalysts that exhibit high capacity for incorporating oxygen during the short pulses of oxygen, (fuel cuts) and an accentuated ability to a complete release of O_2 during the long periods under non-oxidant atmosphere (stoichiometric mode) would be highly desirable.

The present work focuses on a preliminary study of the behaviour of several ceria-praseodymia mixed oxides under $^{18}O_2$ pulses in an attempt to investigate their ability to interact with oxygen, (uptaking/releasing/exchanging) with their own lattice oxygen, under conditions which could simulate those existing in these exhaust gases. For this purpose, several Ce-Pr mixed oxides prepared by two different routes were synthesized in order to explore their responses under two consecutive isotopic $^{18}O_2$ pulses. The final goal is to stablish relationships among the physico-chemical properties of the catalysts, their capacities to interact with oxygen and their soot combustion activities under oxygen pulses.

Experimental/methodology. For this study, $Ce_{1-x}Pr_xO_{2-\delta}$ mixed oxides, (where x is 0.4, 0.6, 0.8 and 1) were prepared by two conventional methods (co-precipitation and intimate mixture of the metallic precursors) [1]. The solids obtained were calcined for 1 hour at 500°C. Pure ceria and a home-made 1.9%Pt/11.5%Ba/1.4%K/γ-Al_2O_3 catalyst were also analysed for comparative purposes. $^{18}O_2$ pulse experiments at several temperatures of interest (200-500°C) were performed (8.5 psi of pressure). The experiments were carried out with 100 mg of catalyst diluted with 180 mg of SiC. Previously, the catalysts were treated under He at 500°C (the temperature of preparation), in an attempt to simulate a long period of non-oxidant atmosphere. The same experiments were repeated in the presence of soot using a 1:20 soot:catalyst ratio (*loose-contact mode* of mixing).

Results and discussion. The results obtained with the all the catalysts illustrate that the extent of oxygen uptake and isotopic products distribution ($^{16}O_2$, $^{18}O^{16}O$, $^{18}O_2$) are dependent on the catalyst composition and the preparation procedure. It should be mentioned that the Pt-catalyst does not exhibit O_2 uptake whatever the temperature tested, meanwhile the Pr-containing catalysts present several extents of O_2 uptake. In general, the catalysts prepared by the Co-precipitation method exhibit higher uptake capacities than those prepared by the Direct calcination method, whatever the composition compared. Concerning soot combustion activities under these transient conditions, the whole experiments conducted point out that the presence of high Pr contents in the mixed oxides as well as high BET surface areas are crucial to achieve high soot combustion activities under these demanding conditions. The pattern of the profiles is very sensitive to the nature of the catalyst, since pure ceria exhibits sharp profiles of $C^{16}O_2$ emission during the $^{18}O_2$ pulse and fast decay of the $C^{16}O_2$ signal during the long inert period, meanwhile the Pr-containing mixed oxides exhibit wider $C^{16}O_2$ peaks with prolonged tails, thus suggesting a pronounced intervention of the active oxygen species even during the inert period. Conversely, Pt-catalyst present a very low soot combustion activity with null intervention of active oxygen species after finishing the $^{18}O_2$ pulses.

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Operando characterization techniques and smart catalyst design as a tool for strategy development towards noble metal content reduction

D. Gashnikova[1], F. Maurer[1], P. Dolcet[1], M. Casapu[1*], J.-D. Grunwaldt[1*]

[1]*Instituite for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany, *maria.casapu@kit.edu; *grunwaldt@kit.edu*

Introduction.

Noble metal based clusters or particles supported on high surface area metal oxides e.g. CeO_2, TiO_2 or Al_2O_3 belong to the essential compounds that are used in emission control catalysis both in mobile and stationary conditions. Due to their limited availability, a drastic reduction of noble metal loading is highly desirable, which, nevertheless, should not negatively affect their catalytic activity. As we have shown in our previous studies, noble metal catalysts, however, rarely retain their original structure under transient reaction conditions. [1-3] For this reason, a correct identification of active sites using a combination of complementary *operando* characterization techniques is crucial for establishment of proper structure-activity correlations. X-ray absorption spectroscopy (XAS) is ideal as it can give insight into the transformation from single sites to clusters or particles and vice versa. Herein, we aimed at a smart catalyst design to minimize a negative effect of structural changes occurring under reactive atmosphere, and to increase catalyst stability including reactivation for long-term applications under transient conditions.

Experimental/methodology.

In this study, a range of Pd/CeO_2-based catalysts with low Pd loading (≤1 wt.%) were synthesized by flame spray pyrolysis (FSP). The catalytic activity of Pd/CeO_2 samples was investigated during CO oxidation reaction (1000 ppm CO, 8% O_2 in N_2). For activity tests, the sieved catalyst (125-250 µm) was and placed in a plug-flow reactor and a Fourier transform infrared spectrometer (Multigas FTIR Spectroscopy, MKS) was used for product analysis at the reactor outlet. For *operando* X-ray absorption spectroscopy (XAS) measurements, a quartz glas microreactor with plug-flow geometry was used. The XAS spectra were recorded under transient conditions at the Pd K edge in fluorescence mode at the SAMBA beamline (SOLEIL). Similar to the catalytic tests in the lab, the gas composition was analyzed with on-line FTIR spectroscopy at the reactor outlet.

Results and discussion.

Using FSP as a synthesis method, very homogeneous Pd-catalysts with a high surface area in the range of 200250 $m^2\ g^{-1}$ were obtained according to *ex situ* characterization results (XRD, BET, HAAD-STEM, *ex situ* XAS). The activity tests indicate a high CO oxidation activity for the low-loaded Pd-catalysts, with a temperature of full conversion way below 150 °C. Moreover, this high activity remained unchanged during subsequent light-off/light-out cycles, showing the high stability of the FSP-prepared samples. Using a combination of complementary *operando* techniques, we were furthermore able to identify the active noble metal structure, and followed its evolution under reaction conditions. The results of this study underline the key role of *operando* characterization together with advanced synthesis methods for the knowledge-based catalyst design of low-loaded noble metal catalysts in the future.

Acknowledgments

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Effect of copper doping in the catalytic performance of $Ba_{0.9}A_{0.1}MnO_3$ (A=Ce, La) perovskites for GDI soot oxidation

N. Ghezali, A. Díaz Verde and M. J. Illán Gómez
Carbon Materials and Environment Research Group. Inorganic Chemistry Department.
University of Alicante. Spain. gn11@alu.au.es

Keywords: perovskite, barium, manganese, Cerium, Lanthanum, soot oxidation, GDI engines.

Introduction.

Soot and NOx emitted by automotive engines are responsible for severe environmental and health problems. It has been proposed that perovskites type mixed oxide are a feasible alternative to PGM-based catalysts because promote soot oxidation thanks to its particular properties that can be modulated by either synthesis procedure, composition (different A and B cations) and the partial substitution of A and/or B cations [1]. In a previous study, the authors concluded that $BaMn_{0.7}Cu_{0.3}O_3$ is the best catalyst for diesel soot removal from a series of $BaMn_{x-1}Cu_xO_3$ perovskites, due to its high amount of oxygen vacancies [2].In this work, $Ba_{0.9}A_{0.1}MnO_3$ and $Ba_{0.9}A_{0.1}Mn_{0.7}Cu_{0.3}$ O_3 (A= Ce, La) perovskites have been synthesized, characterized, and tested as catalysts for GDI soot oxidation.

Experimental/methodology.

The synthesis of the perovskites (named BM/BMA, and BMC/BMCA, A=Ce, La), was carried out by sol-gel method in an aqueous medium, using citric acid as a chelating agent. For sample characterization, BET, XRD, H_2-TPR, XPS and O_2-TPD have been employed. The catalytic activity for GDI soot oxidation has been studied under simulated GDI operation conditions (1% or 0% O_2 in He).

Results and discussion.

Characterization results revealed that copper is partially introduced into the structure of BM perovskite, showing BMCLa the highest amount of surface copper and BMCCe, the lowest one. BMCA shows, respect to BM, a slightly increase in the amount of oxygen surface defects, in the reducibility of manganese and in the amount of oxygen desorbed during an O_2-TPD. In Figure 1, as an example, the Temperature Programmed soot conversion profiles in 1% O_2 for catalysts are shown. Note that the doping with copper only increases the soot conversion respect to BM for BMCLa perovskite.

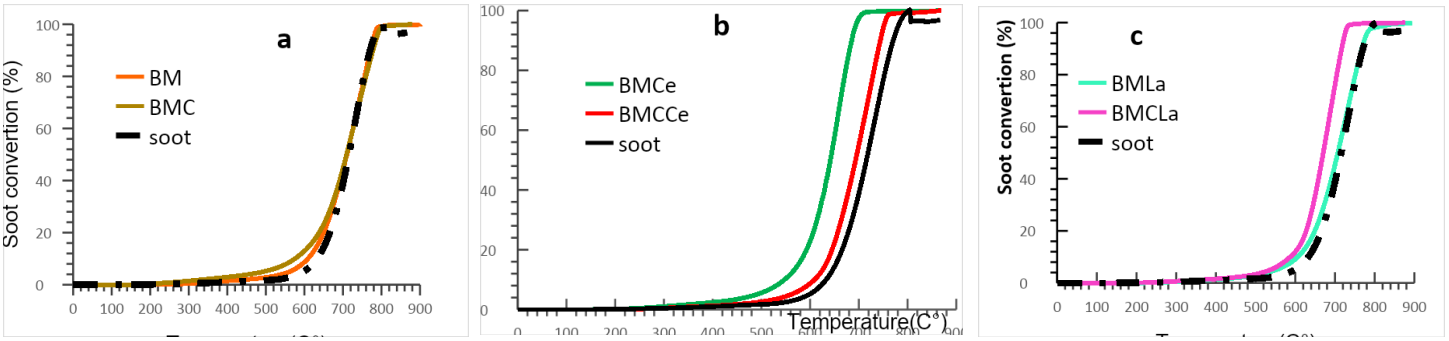

Figure 1 (a,b,c). TPR soot conversion profiles for BMA and BMCA in 1%O_2.

Acknowledgements

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Catalytic oxidation of Cl-VOCs over nanostructured cobalt oxide catalysts

A. Gil-Barbarin[1], J.I. Gutiérrez-Ortiz[1], R. López-Fonseca[1], B. de Rivas[1]

[1] *Chemical Engineering Department, Faculty of Science and Technology, University of the Basque Country/EHU, Bilbao, Spain.*

*amaya.gil@ehu.eus

Introduction

Catalytic oxidation of chlorinated VOCs is presented as an optimal strategy for the control of the emissions of this type of pollutants. In this sense, the choice of a suitable catalyst (active and selective towards deep oxidation products) is essential to achieve the desired target. Catalysts based on transition metal oxides, especially cobalt oxide, have proven to be effective in a wide range of catalytic reactions. On the other hand, over the last few years, materials with hollow nanostructure have received great attention due to their excellent performance in different applications [1]. Hollow nanostructures (nanotubes) can be obtained under mild conditions and without costly templates and corrosive acids following the Kirkendall effect. Thus, this study examines Co_3O_4 catalysts with a controlled 1D nanomorphology and evaluates their performance in the oxidative gas phase removal of 1000 ppm of Cl-VOCs (vinyl chloride and 1,2-dichloroethane as model compounds).

Experimental/methodology

Bulk Co_3O_4 samples were synthesised following three precipitation routes based on the Kirkendall effect:

Co_3O_4-S: an oxalic acid solution was mixed with a cobalt chloride solution under stirring for 3 h. The precursor was filtered, washed, and dried. Then, it was dispersed in EtOH and an ethanolic solution of NaOH was added dropwise. After 3 h under stirring the product was filtered, washed, dried, and calcined in air at 500 ºC for 4 h.

Co_3O_4-A: an aqueous solution of ammonia was added drop by drop to an ethanolic solution of cobalt acetate and the mixture was kept under stirring for 6 days. Afterwards, the solid was centrifugated, washed, dried, and calcined in air at 290 ºC and 500 ºC for 4 h.

Co_3O_4-U: two ethanolic solutions of cobalt acetate and urea were mixed under stirring at 65 ºC for 4 h. Then, the precursor was filtered, washed, dried, and calcined under controlled atmosphere (5% O_2/He) at 350 ºC and 500 ºC for 4 h.

Results and discussion

Cobalt oxide catalysts with a hollow nanotube structure were obtained as confirmed by SEM. Among the different samples, the Co_3O_4-U oxide exhibited the highest surface area (19 $m^2\ g^{-1}$) and the smallest crystallite size (22 nm). Moreover, H_2-TPR and XPS results revealed a higher amount of Co^{2+} species in this oxide, both at bulk and surface level. Additionally, the presence of Co^{2+} species is usually connected to the formation of low coordination defect lattice oxygen sites. This assumption was confirmed by Raman spectroscopy, as a shift of the A_{1g} vibration towards lower frequencies is an indication of a highly defective structure [2]. In agreement with these results, the catalytic activity runs also clearly evidenced the highest efficiency of the Co_3O_4-U sample for the oxidative removal of VC and DCE (T_{50} of 260 ºC and 325 ºC, respectively). Accordingly, this structure-activity relationship was consistent with the highest specific rate of the Co_3O_4-U sample (Figure 1). In conclusion, the reason for this improved performance was the formation of surface oxygen defects, due to a high concentration of Co^{2+} that promoted the generation of active oxygen species along with the adsorption capacity of the chlorocarbons.

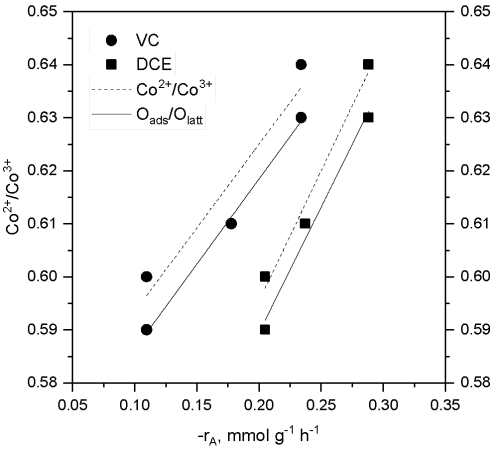

Figure 1. Relationship among the reactivity and the Co^{2+}/Co^{3+} and O_{ads}/O_{latt} molar ratios.

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Oxidation of 1,2-dichlorobenzene (o-DCB) with MnO_X-CeO_2 formulation

J.A. Martín-Martín, M.P. González-Marcos, A. Aranzabal, J.R. González-Velasco

The University of the Basque Country, UPV/EHU*, Bilbao, Spain*

Introduction.

MnO_X-CeO_2 catalytic formulation has been proposed in many studies as an excellent catalyst for low temperature SCR [1], which would avoid the typical reheating of gases fed to the current SCR units in tail-end position. This formulation is also reported to be active in catalytic oxidation reactions [2], which means the posibility of abating simultaneously NO_X and chlorinated VOCs in the same catalytic unit. The aim of this work is to evaluate the MnO_X-CeO_2 formulation in o-DCB oxidation (model compound of PCDD/Fs).

Experimental/methodology.

MnO_X-CeO_2 catalysts were prepared by co-precipitation, adding an ammonium carbamate solution (precipitating agent) unil reaching a pH=9. Calcination was carried out in static air at 500 ºC (1 ºC/min). For catalytic activity tests, 1.5 g of catalyst and a feeding stream (2 L/min) composed of o-DCB (100 ppm), O_2 (10%) and Ar to balance were used.

Results and discussion.

The results of light-off experiments concluded that MnO_X-CeO_2 formulation is active for o-DCB oxidation. The increase in Mn content shifts the conversion profile to lower temperatures. Nonetheless, the presence of Ce also plays an important role, especially in the low temperature range (<300 ºC). The better catalytic activity of the catalysts with high Mn content is related to, on the one hand, the promotion of morphological properties, and, on the other hand, the co-existence of two crystalline phases at the structural level (mixed oxide phase and seggregated Mn_2O_3) whose synergy improves the oxygen mobility/storage and redox properties.

The analysis of adsorbed species by in-situ FTIR showed that the first steps of oxidation reaction are two nucleophilic substitutions followed by the cleavage of aromatic ring. After these steps, a different distribution of intermediate species with temperature was observed, which suggests oxidation reaction occurs differently with temperature. Thus, the main species at low temperature were phenate and maleate, wheras acetate and formate species were the ones at high temperature.

In order to evaluate whether oxidation reaction performed with MnO_X-CeO_2 formulation occurs differently with temperature, time on stream (TOS) experiments were carried out in the low and high temperature range. The results showed a strong catalyst deactivation at low temperature due to the deposition of chlorine and carbonaceous matter. TOS experiments also evidenced a change in the product distribution at high temperature, in which CO and chlorinated organic compounds were produced (to a lower extent than CO_2) after a period of time. Interestingly, this fact did not occur in the low temperature range, where the only reaction product was CO_2 (together with water).

Therefore, both FTIR and TOS results suggest a change in oxidation reaction pathway with temperature. To understand this fact, it is important to note the results of characterization: MnO_X-CeO_2 catalyst was composed of two phases with a different Mn and Ce interaction degree and, consequently, different oxidative capability. This fact is proposed to provide the catalyst active sites with diferent activity. Thus, the active sites with higher oxidative capability mainly contribute to oxidation reaction. However, they are strongly deactivated. At high temperature, the active sites with lower oxidative capability become active, but favouring the oxidation of intermediate species more slowly. This fact facilitates chlorination reactions (at high temperature, Cl is more weakly adsorbed) leading to chlorinated by-products, whose number of carbons, interestingly, matchs with that of intermediate species identified at this condition.

Acknowledgements

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Design of subsurface single-atom catalysts for oxidation chemistry

Xuze Guan,[1] *Feng Ryan Wang*,[1*]

[1]*Department of Chemical Engineering, University College London, Roberts Building, Torrington Place, London WC1E 7JE, UK*

**e-mail: ryan.wang@ucl.ac.uk*

Introduction.

Single-atom catalysts (SACs) have become the research frontier in heterogeneous catalysis because of their high atom utilization and special metal-support interactions. The locations of isolated metal atoms on supports determine their catalytic performances[1,2]. Typically, single metal atoms are anchored onto the support surface. Applications of surface single-atom catalysts are usually hampered by limited catalyst stability, which is caused by sintering[3,4]. Therefore, understanding the structure-activity relationship of SACs under various reaction conditions, and exploring and controlling the location of single atoms that is resistant to sintering, are crucial to the design of SACs for practical applications.

Experimental/methodology.

The CuO-Fe_2O_3 catalyst with 1wt% Cu was prepared first by the coprecipitation method. The Cu sites were atomically dispersed over Fe_2O_3. Cu single sites were introduced onto Fe_2O_3 supports to tune the surface redox ability and to anchor formed NO during the reactions[5]. Then, the Cu single sites were immersed into the subsurface *via* ball milling.

Results and discussion.

Here, we inserted the single Cu atoms into the subsurface of Fe_2O_3 support (Fig. 1a), showing drastically different dynamics and adsorption behaviours under the reaction conditions. Extended X-ray absorption fine structure (EXAFS) spectra indicate atomically dispersed Cu. An increase in the coordination number of Cu–Fe (from 2.2 to 2.7) indicates Cu single atoms enter the interior of the Fe_2O_3. The X-ray photoelectron spectroscopy (XPS) exhibited the Cu signal of the fresh catalyst. In comparison, the Cu in the ball-milled catalyst cannot be measured by XPS, indicating the isolated Cu atoms were not on the surface of Fe_2O_3. Compared with surface Cu single atoms, subsurface Cu single atoms show a high resistance against sintering. After NH_3 pretreatment, the N_2 selectivity decrease significantly for the surface single-atom catalyst, while the subsurface Cu single-atom catalyst is much more stable and active for NH_3 oxidation (Fig. 1b,c). The ability to control the single-atom location opens promising perspectives to turn reducible oxides into reactive materials in oxidation reactions.

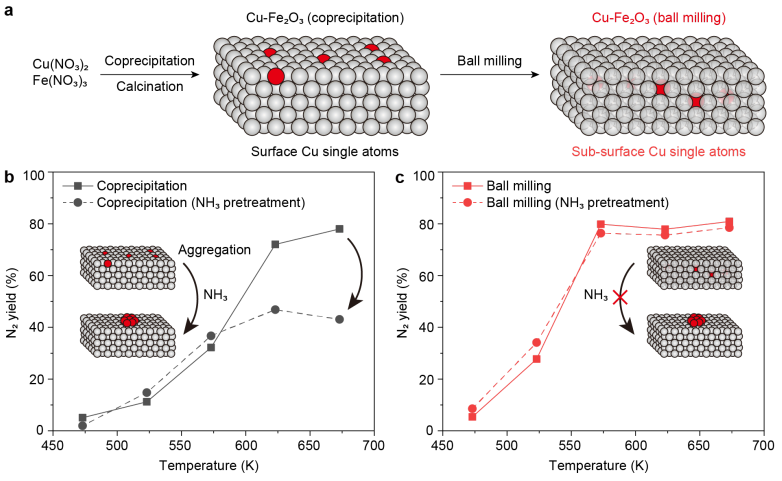

Figure 1. Synthetic scheme and ex-situ characterizations of catalysts. a, Schematic illustration of immersing Cu into Fe_2O_3 *via* ball milling. **b**, N_2 yield of 1wt% CuO-Fe_2O_3 (coprecipitation) before and after NH_3 pre-treatment. **c**, N_2 yield of 1wt% CuO-Fe_2O_3 (ball milling) before and after NH_3 pre-treatment.

Acknowledgments

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Modulation of the redox capacity of copper by calcium during the reduction of NO by CO and Naphthalene

J. Herrera[1], G. Aguila[2], S. Guerrero[1*]

[1]*Universidad de los Andes, Santiago, Chile*
[2]*Universidad Andres Bello, Santiago, Chile*
[*]*sguerrero@uandes.cl*

Keywords: NO reduction, Copper catalyst, CO, Naphthalene

Introduction. The present study uses CO and naphthalene to reduce nitric oxide to N_2 in the presence of O_2. The challenge in this reaction is to prevent CO and naphthalene from being oxidized instead of being used as NO reducers. This study will show that the combination of copper and calcium on core-shell support, $YCeO_2$@TiO_2, can effectively modulate the oxidation of the reducing agents favoring the selectivity to N_2.

Experimental/methodology. A core-shell $YCeO_2$@TiO_2 support was prepared by a reverse micelle procedure and further sequentially wet-impregnated with copper and calcium. The catalytic bed consisted of a proper amount of catalyst deposited on a mineral wool bed inside a quartz tube reactor (1 cm I.D.) and set in a split-oven. The simulated gaseous mixture (GHSV = 10,000 h^{-1}) consisted of 500 ppm naphthalene, 500 ppm NO, 1% CO, and 10% O_2, balanced in He, flowing at 50 cc/min. The outlet from the reactor was screened to monitor the presence of NO, NO_2, N_2O, CO, and naphthalene, among others, by using infrared spectrometry, gas chromatography, and mass spectrometry.

Results and discussion. Figure 1A shows that the Ca/Cu/$YCeO_2$@TiO_2 catalyst is highly active fully converting CO and naphthalene, with NO reaching a maximum of 60% conversion to N_2 at 276°C. The reduction profile shown in Figure 1B shows how the addition of calcium displaces the copper reduction to high temperatures and decreases the overall H_2 consumption when compared with the calcium-free sample (Cu/$YCeO_2$@TiO_2). The latter suggests a higher Ca-O-Cu interaction which makes it more difficult to reduce the copper phase. Therefore, the addition of calcium might be used to modulate the redox capacity of copper to avoid the direct oxidation of the reducing agent instead of reacting with NO.

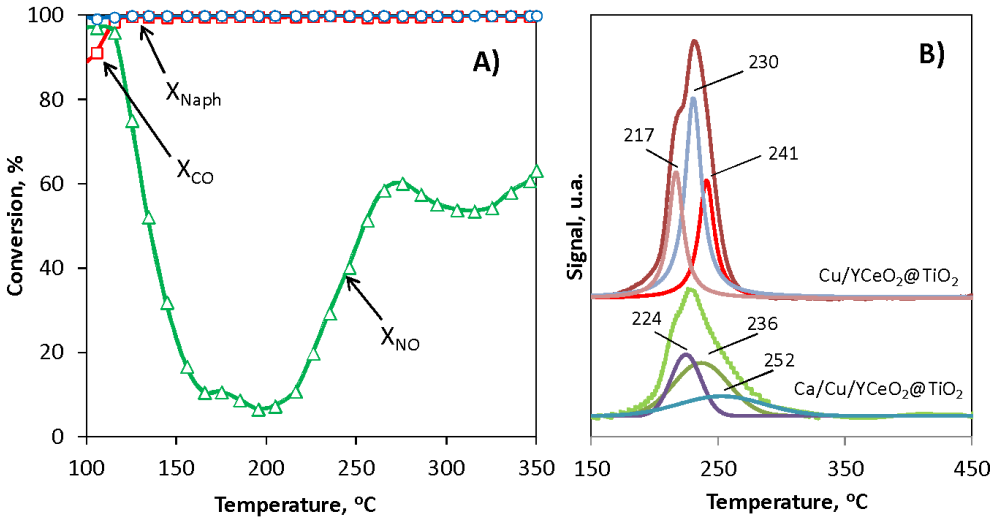

Figure 1. A) Reduction of NO with CO and naphtalene on Ca/Cu/$YCeO_2$@TiO_2 in the presence of O_2 and B) H_2-TPR on Cu/$YCeO_2$@TiO_2 and Ca/Cu/$YCeO_2$@TiO_2.

Acknowledgments
The Chilean National Science and Technology Research Fund, FONDECYT REGULAR project 1220582, is greatly acknowledged for funding this work.

Alkaline Earth Containing Yttrium Oxide Based Catalysts for High-Temperature NO Decomposition Reaction

K. Takenaka, Y. Hayashi, Y. Nishida, M. Haneda*

Advanced Ceramics Research Center, Nagoya Institute of Tehnology, Tajimi, Japan

Keywords: NO decomposition, Alkaline earth additive, Yttrium oxide, Transition metal oxide additive

Introduction. Among the various catalytic NO_x removal technologies, NO decomposition is regarded as the most ideal method. This is because reducing agents such as NH_3 for NO reduction are not necessary. We have so far investigated yttrium oxide-based catalysts, and found that co-doping of Ba and CeO_2 into Y_2O_3 is quite effective to achieve high NO decomposition activity at 900ºC [1,2]. However, its activity and stability in higher temperature region above 1000 ºC is still problem. In this study, we have investigated the additive effect of transition metals to improve the activity and stability of $Ba/Ce/Y_2O_3$. The effect of alkaline earth elements was also investigated to gain insight into the improvement of the activity under the realistic condition in the presence of CO_2.

Experimental. All the catalysts were prepared by coprecipitation method. The composition was 8mol% alkaline earth (A: Mg, Ca, Sr, Ba), 10 mol% CeO_2 and 3mol% transition metals (M: Mn, Fe, Co, Ni, Cu), 79mol% Y_2O_3 as oxide. The resulting precipitate was dried at 110°C, and then calcined at 1000°C for 5h in air. The catalyst is hereinafter referred to as $ACeM/Y_2O_3$. NO decomposition reaction was carried out with a fixed bed flow reactor by passing a reaction gas composed of 0.1% NO diluted He to the catalyst bed ($W/F=1.0 g \cdot s \cdot cm^{-3}$). The steady state activity was evaluated at each temperature in the range of 900 – 1100°C. As the characterizations, O_2-TPD and CO_2-TPD were performed.

Results and discussion. Fig.1 shows the effect of transition metal on the NO decomposition activity of $BaCe/Y_2O_3$. Among the additives, Fe was found to be the most effective. $BaFeCe/Y_2O_3$ showed quite high activity in 900 - 1100°C temperature range. From O_2-TPD measurements, the essential role of Fe was to promote oxygen desorption. The activity of Fe-doped Ce/Y_2O_3 was found to be strongly dependent on the alkaline earth element. The effective additive was Ba and Sr. In order to gain information on the difference in the catalytic performance of Ba- and Sr-doped catalyst, the catalytic activity was evaluated in the presence of 1% CO_2. It was dound that Ba- and Sr-doped catalysts shows similar catalytic activity, although Ba-doped catalyst is quite effective in the absence of CO_2. CO_2-TPD suggested the advantage of Sr-doped catalyst by the presence of relatively weak basic sites.

Fig.1 Effect of transition metal additive on the NO decomposition activity of $BaCe/Y_2O_3$.

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Understanding the impact of aging conditions on the thermal deactivation of three-way catalysts

Sarina-Lena Heck[1*], Paolo Dolcet[2], Gülperi Nails[1], Jan-Dierk Grunwaldt[1,2], Maria Casapu[1*]

[1]*Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*

[2]*Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany*

[*]*sarina-lena.heck@kit.edu, maria.casapu@kit.edu*

Introduction.

Despite their extensive worldwide use, thermal deactivation and processes occurring on an atomic scale during long-term application of emission control catalysts are not yet completely understood. Typically, segregation, sintering, solid-state reactions and encapsulation are observed thus affecting the properties of both the active species and the supports.[1,2,3] Common support materials for three-way catalyst are oxides like γ-Al_2O_3 or CeO_2-ZrO_2; γ-Al_2O_3 exhibits a high surface area, while CeO_2-ZrO_2 are applied for their oxygen storage capacity to balance out fluctuations in the stoichiometric air-to-fuel ratio needed for an optimal performance.[2,4] Additionally, they sustain the noble metal dispersion during high temperature utilization. For the noble metals, i. e. Pd, Pt and Rh, commonly employed in the three-way catalyst, thermal deactivation processes are known to not only dependent on the aging temperature but also on the applied gas atmosphere.[5,6] Our study aims at elucidating the behavior of Rh and Pd during thermal deactivation by systematic catalyst preparation, testing and in-depth *ex situ/in situ* characterization.

Experimental/methodology.

A series of different Pd- and Rh-catalysts supported on CeO_2-ZrO_2 were prepared by incipient wetness impregnation and the resulting powders were aged under oxidizing or inert conditions. The structural öfeatures of the resulting samples were revealed by complementary *ex situ* and *in situ* characterization techniques including XRD, H_2-TPR, XPS, N_2-physisorption and XAS measurements. Several light-off/light-out cycles were performed while monitoring the gas mixture with and FTIR spectrometer (MKS) to evaluate the catalytic activity.

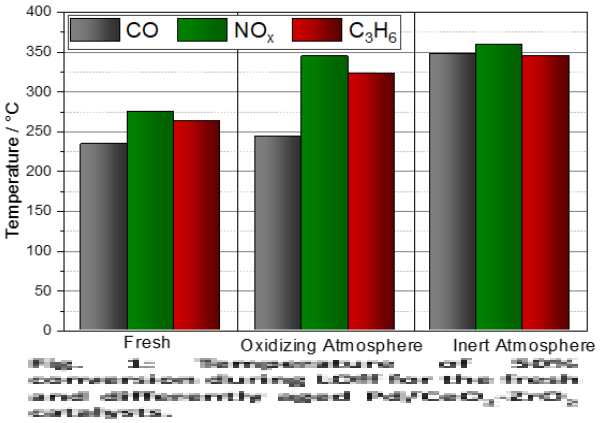

Fig. 1: Temperature of 50% conversion during LOff for the fresh and differently aged Pd/CeO_2-ZrO_2 catalysts.

Results and discussion.

While studying the impact of the aging conditions on the catalytic activity, a major drop in the conversion of all three pollutants CO, NO_x and C_3H_6 was observed for the samples exposed to high temperatures and inert atmosphere. In contrast, pretreating the catalyst in oxidizing atmosphere mainly affects NO_x and C_3H_6 conversion, whereas the catalytic activity towards CO oxidation was only slightly impaired. XRD measurements demonstrated a severe sintering of the support material independent of the aging condition; *ex situ* XANES and EXAFS characterization revealed that aging in oxidizing atmosphere promotes the formation of larger oxidized noble metal particles.

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Facile one-pot synthesis of Fe-UZM-35 catalysts for ammonia selective catalytic reduction

Xuechao Tan, Shoute Zhang, Suk Bong Hong*

Center for Ordered Nanoporous Materials Synthesis, Division of Environmental Science and Engineering, POSTECH, Pohang 37673, Korea
**Corresponding Author's E-mail address: sbhong@postech.ac.kr*

Keywords: Fe-UZM-35; Interzeolite conversion route; One-pot synthesis; High reproducibility; NH_3-SCR

Introduction. Fe-UZM-35 with MSE topology of particular interest in that its low-temperature activity in NH_3-SCR is best among the Fe-zeolites known to date[1]. However, owing to the narrow crystallization field, the synthesis of this large-pore zeolite starting from amorphous reagents in the presence of dimethyldipropylammonium ions as an organic structure-directing agent is often non-reproducible[2]. Moreover, Fe^{2+} exchange in zeolites requires the prevention of Fe^{2+} oxidation to trivalent iron species such as FeO(OH), which cannot be easily introduced into the zeolite pores during ion exchange [3], requiring the use of inert N_2 atmosphere. Here we describe novel synthesis routes to UZM-35 and Fe-UZM-35.

Experimental/methodology. The interzeolite conversion (IZC) synthesis of UZM-35, which uses ultra-stable Y (USY) zeolites as the sole source of Si and Al, as well as the one-pot-synthesis of Fe-UZM-35, was performed using aluminosilicate gels with the composition $4.50DMDPAOH{\cdot}0.25Na_2O{\cdot}0.75K_2O{\cdot}xFe^{II}O{\cdot}yAl_2O_3{\cdot}10.0SiO_2{\cdot}155H_2O$, where x is varied between $0 \le x \le 0.50$ and $0.017 \le y \le 0.067$, respectively. If required, a small amount of previously synthesized and calcined UZM-35 (4 wt% of USY used) was added as seed crystals, respectively. The final mixture was placed into a 45 mL Teflon-lined autoclave and heated under static conditions at 170 °C for 0.5-7 days.

Results and discussion. We were able to synthesize pure UZM-35 by combining the IZC route with the seeding method, using USY zeolites as both Al and Si-sources in the presence of DMDPA as an OSDA (**Figure 1a**). We were also successful in the one-pot-synthesis of Fe-UZM-35 (**Figure 1b**), which is much more convenient and reproducible than the post-synthetic preparation of iron-exchanged UZM-35; there is no need for careful iron exchange under N_2 atmosphere and repeated calcination steps. More importantly, the NH_3-SCR activities of one-pot-synthesized and post-synthetically exchanged Fe-UZM-35 zeolites with similar Fe/Al ratios (ca. 0.23) were found to be essentially identical to each other in the reaction temperature range studied (**Figure 1c**).

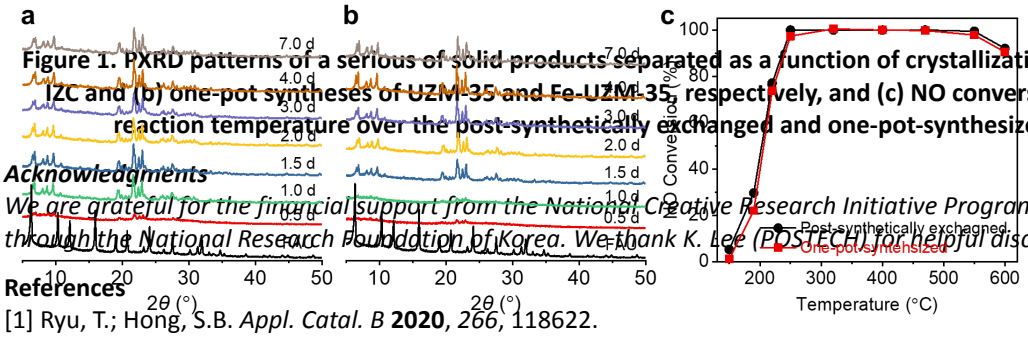

Figure 1. PXRD patterns of a serious of solid products separated as a function of crystallization time during the (a) IZC and (b) one-pot syntheses of UZM-35 and Fe-UZM-35, respectively, and (c) NO conversion as a function of reaction temperature over the post-synthetically exchanged and one-pot-synthesized Fe-UZM-35

Acknowledgments

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Beta zeolite (BEA)-based catalysts for the removal of N_2O from flue gas of ammonia-powered ships

R. Chand[1], J. M. Christensen[1], B. B. Hansen[1], M. Brorson[2], A. D. Jensen[1*]

[1]*Technical University of Denmark (DTU), Department of Chemical and Biochemical Engineering, Kgs. Lyngby, Denmark*
[2]*TOPSOE A/S, Kgs. Lyngby, Denmark*
[*] *aj@kt.dtu.dk*

Keywords: nitrous oxide, ammonia, shipping, catalytic decomposition, selective catalytic reduction

Introduction. According to the International Maritime Organization (IMO), present shipping activities are responsible for ~2.5% of global GHG emissions and this contribution is expected to increase in the coming years due to increasing global trade. Taking these into consideration, the IMO has come to an agreement to work towards certain ambitious targets such as reducing GHG emissions from international shipping by at least 50% by 2050, decreasing carbon intensity by at least 40% (compared to a benchmark set in 2008) by 2030 and achieving complete decarbonization of the shipping sector by the end of the 21st century (1).

The first step towards achieving these goals is to come up with an alternative, carbon-free fuel. Ammonia (NH_3) is one such promising candidate for fueling ship engines because, unlike hydrogen, ammonia can be stored in liquid form at room temperature and low pressure for long-distance voyages. However, it leads to the emissions of NO_x, N_2O (nitrous oxide) and unburnt NH_3, which need to be managed by using a dedicated Exhaust Aftertreatment System (EATS). Among the flue gas species, N_2O has a concerning potential for global warming. N_2O is known to be ~300 times more potent to cause global warming than CO_2 on a per mass basis (2). In addition, N_2O can react with oxygen in the atmosphere to form nitric oxide, which is one of the contributors of ozone layer depletion (2, 3). Anthropogenic sources are responsible for ~35% of N_2O emissions and N_2O concentration in the atmosphere has increased at an alarming rate of ~0.2–0.3%/year in the last century (2). N_2O emissions can be countered by either direct catalytic decomposition into N_2 and O_2 or selective catalytic reduction (SCR) into N_2 and H_2O (2, 4).

In this contribution, we explore the catalytic performance of K-promoted Co/BEA catalysts for the removal of N_2O and compare it to that of commercially available Fe-BEA catalysts. The novelty of this work lies in the use of Co/BEA catalysts, which have been scarcely reported in the literature for N_2O abatement.

Experimental/methodology. Catalytic experiments were carried out in a quartz U-tube reactor using two catalysts – K-Co/BEA and Fe-BEA. The K-Co/BEA catalyst was synthesized via incipient wetness impregnation while the Fe-BEA catalyst was procured from Topsoe A/S. Catalytic decomposition of N_2O was carried out in the presence and absence of water. Further, removal of N_2O was also investigated using ammonia as reductant in the presence of water. The reactions were performed in the range of 150-500 °C.

Results and discussion. For catalytic decomposition, in the absence of H_2O, both K-Co/BEA and Fe-BEA show similar catalytic activity in the temperature range of 400-500 °C. In the presence of H_2O, K-Co/BEA performs much better than Fe-BEA, even though the N_2O conversion for K-Co/BEA reduces by ~50%. Further, with the introduction of NH_3, the N_2O conversion for Fe-BEA shoots up and reaches the highest value observed in any of the experiments, while the final value for K-Co/FEA remains almost unchanged.

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Understanding different zinc species effect on Mn-Ce/CuX catalyst for low-temperature NH_3-SCR reaction: Comparison of $ZnCl_2$, $Zn(NO_3)_2$, $ZnSO_4$ and $ZnCO_3$

Lin Chen [1, 2], Shan Ren[1, *], Tao Chen [1], Xiaodi Li [1], Zhichao Chen [1], Mingming Wang [1], Qingcai Liu [1]

[1]*College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China*
[2]*Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*
** Corresponding author email: shan.ren@cqu.edu.cn(S. Ren)*

Keywords: Mn-Ce/CuX catalyst, different zinc species poisoning, low-temperature NH_3-SCR

Introduction. Nitrogen oxides (NOx), emitted from coal-fired power plants and other nonelectric industries, are one of the main air pollutants to cause harm for human health and environments. [1].The zeolite-based catalysts were widely used in denitration removal reaction [2-4], especially Cu-exchanged zeolite catalysts owing to the high SCR activity [4-6]. Our recent research [7] discovered that the X zeolite supported catalyst performed better low-temperature NO conversion than that of other zeolite catalysts, such as ZSM-5 and Beta zeolites. Then the X zeolite was synthesized from waste BFS using seed methods, and the Mn-Ce co-doping CuX catalyst was prepared via ion exchange and impregnation methods, and it exhibited excellent catalytic activity and SO_2/H_2O resistance [8, 9]. However, owing to the low-temperature catalysts for NH_3-SCR suffering from poisoning effect of heavy metals in the sintering flue gas, herein, the influence of different zinc species ($ZnCl_2$, $Zn(NO_3)_2$, $ZnSO_4$ and $ZnCO_3$) on blast furnace slag-derived Mn-Ce/CuX catalyst for low-temperature NH_3-SCR were compared and studied.

Experimental/methodology. Poisoned catalysts were prepared by impregnating with $ZnCl_2$, $Zn(NO_3)_2$, $ZnSO_4$ and $ZnCO_3$ aqueous solutions, respectively. The catalytic activities of all catalysts were measured, and the physicochemical properties of zinc poisoned catalysts were investigated.

Results and discussion. After zinc species poisoning, catalytic activity decreased significantly in the low temperature range, and the poisoning degree followed $ZnSO_4$ > $ZnCO_3$ > $Zn(NO_3)_2$ > $ZnCl_2$. The Zn salts poisoning catalysts have lower acidity and redox ability compared with fresh Mn-Ce/CuX catalysts, resulting in the lower SCR activity. Furthermore, all the catalysts were governed by both Langmiur-Hinshelwood (L-H) and Eley-Rideal (E-R) mechanism via *in situ* DRIFTS spectra, the possible mechanism for different zinc species poisoning on Mn-Ce/CuX catalyst was summarized as well.

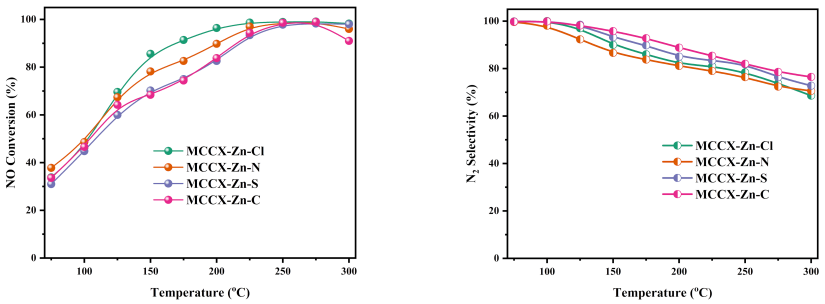

Fig.1. NH_3-SCR activity of MCCX-Zn-Cl, MCCX-Zn-N, MCCX-Zn-S and MCCX-Zn-C catalysts: (a) NO conversion with temperature; (b) N_2 selectivity with temperature.

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Novel nanostructured Pd/Co-alumina materials for the catalytic oxidation of atmospheric pollutants

E.F. Iliopoulou*, E. P. Pachatouridou, A.A. Lappas

Chemical Process & Energy Resources Institute (CPERI), Centre for Research & Technology Hellas (CERTH), Thermi, Thessaloniki, Greece

Corresponding Author's E-mail address: eh@certh.gr

Keywords: Cobalt oxide, CO oxidation, catalyst morphology

Introduction. Supported noble metals such as Pd and Pt are known for their superior performance in catalytic oxidation of CO, however, their high cost limits their extended use in commercial applications. Transition and rare-earth metal oxide catalysts have received considerable attention due to both their high efficiency and low cost. Cobalt oxide is known as the most active catalyst for CO oxidation due to its weak oxygen bond strength and high turnover frequency for redox reaction [1]. Lately, a plethora of research studies focus on morphology-dependent nanocatalysis, while the synthesis method seems to have a crucial effect on the structural properties of catalytic materials (e.g. surface area, oxidation state, dispersion of actives sites, etc). Cobalt-doped alumina nanosheets were prepared as oxidation catalysts by dynamic hydrothermal method, and then further promoted with precious metal Ru or Pd. Cobalt doping imparted the prominent redox ability to irreducible alumina nanosheets and established the strong metal-support interaction and easy activation of gaseous oxygen [2]. In another recent study, Co_3O_4/a-Al_2O_3 catalysts were prepared by a rotary chemical vapor deposition (CVD) method, aiming to the formation of finely dispersed nanoparticles of Co_3O_4 on the a-Al_2O_3 surface, presenting thus high catalytic activity in CO oxidation with the minimum Co content [3]. The present work deals with the development of Co/alumina (promoted or not with minimum Pd amounts) materials evaluated as novel oxidation catalysts.

Experimental/methodology. Introduction of Co and Pd was realized applying either the conventional wet impregnation (WI) or the advanced spray impregnation (SI) technique towards the synthesis of core-shell catalytic nanostructures to secure chemical/thermal stability of active site on the catalyst carrier. The physicochemical characteristics of as-synthesized materials were evaluated by various complimentary, conventional and advanced techniques (N_2 Physisorption, XRD, H_2-TPR, O_2-TPD, SEM and TEM) to elucidate differences between synthesis methods. The catalytic CO oxidation efficiency was evaluated in the 150-500°C temperature range in a fixed-bed reactor, using a feed of 1% CO, 1% or 10% O_2, in He (GHSV: 40000 h^{-1}).

Results and discussion. Pd/Co-alumina catalysts synthesized by the spray impregnation method showed improved CO oxidation efficiency, due to their optimum physicochemical properties and mainly their enhanced reducibility related with better dispersion of Co and Pd active sites 0.5Pd-1Co/Al-SI was the most efficient catalyst presenting T50%= 170°C and achieving ~100% CO conversion at 190°C (Figure 1). Pd incorporation is also attempted via SI, targeting to even lower Pd content, while selected catalytic materials are also investigated as methanol oxidation catalysts.

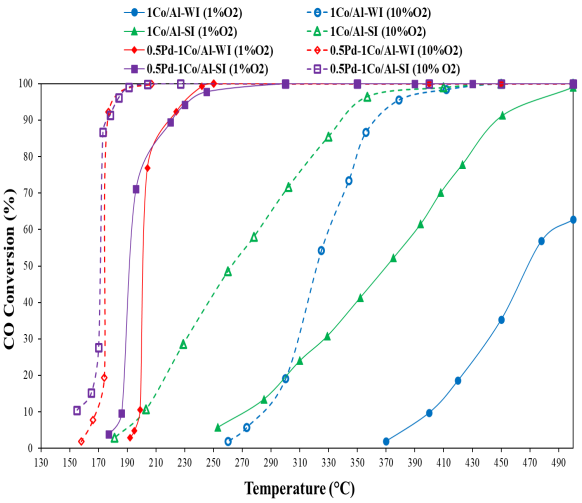

Figure 1. *CO conversion (%) vs. temperature for all (Pd)Co/Al catalysts.*

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Potential catalysts for conversion of nitrogen oxides based on porous silica spheres modified with copper or iron cations

A. Jankowska[1*], A. Kowalczyk[1], M. Rutkowska[1], M. Michalik[2], Z. Piwowarska[1] and L. Chmielarz[1]

[1]*Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30–387 Kraków, Poland*
[2]*Jagiellonian University, Institute of Geological Sciences, Gronostajowa 3a, 30–387 Kraków, Poland*
[*]*aleksandra1.jankowska@uj.edu.pl*

Introduction. The reduction of nitrogen oxides (NO_x) emissions from stationary sources is most often achieved by the use of the technology of selective catalytic reduction of NOx with ammonia (NH_3-SCR). Nevertheless, the commercially used NH_3-SCR catalyst is effective only in a relatively narrow temperature range (300-400°C), which limits its use outside the temperature window of its effective operation.[1] To meet the requirements of modern NH_3-SCR installations it is necessary to design a new generation of catalytic systems. For this purpose, mesoporous spherical MCM-41 was functionalized with transition metals (copper or iron) using an innovative technique of template ion-exchange (TIE).[2]
Experimental/methodology. The obtained materials were tested in the role of NH_3-SCR catalysts and the influence of their intrinsic properties on the catalytic performance was analysed using various characterization methods, including e.g. P-XRD, low-temperature N_2-sorption, ICP, UV-vis DR spectroscopy.
Results and discussion. The catalytic performance of tested NH_3-SCR catalysts was strictly dependent on the form and aggregation of the deposited metal (Cu or Fe), the control of which was possible with the applied TIE method and its modification. In the case of copper-doped MCM-41, materials containing well-dispersed monomeric copper species were more active in comparison to samples characterized by the presence of bulky copper oxide forms. The effective range of the catalyst work for the most active catalyst was between 200 and 325°C with very high selectivity to N_2 (Figure 1). Iron-modified porous nanospheres were active in the elevated temperature range (350-475°C) of the NH_3-SCR process, indicating a slightly higher activity of small oligomeric iron oxide aggregates (Figure 1). The obtained materials showed promising activity in the low-temperature as well as the high-temperature range of the NH_3-SCR process. Thus, it is an attractive alternative to be used in this process to replace a commercially used V_2O_5-TiO_2 oxide system.

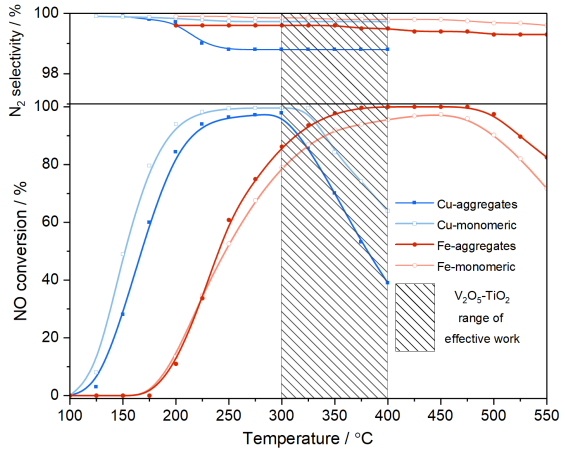

Figure 1. NH_3-SCR catalytic tests obtained for the spherical MCM-41 modified with Cu or Fe with various degrees of aggregation and comparing them with the window of effective operation of the commercial V_2O_5-TiO_2 system.

Acknowledgments
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Ru as cost-effective alternative for Rh in TWCs

Pragati Joshi*[1], Marcus Bonifer[1]

[1] *Heraeus Precious Metals GmbH & Co.KG, Business Unit Catalysts*

Heraeusstr. 12-14, 63450 Hanau, Germany

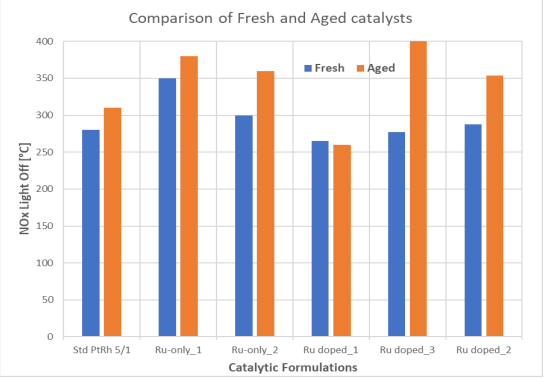
**pragati.joshi@heraeus.com*; marcus.bonifer@heraeus.com

Introduction

Global air pollution caused by various industrial as well as human activities has led to major health issues and damage to the environment. As a result, scientists all over the world came up with catalytic solutions to overcome the emission problems. Development of Three-Way Catalyst (TWC) technology is the key development in maintaining air quality regulations for gasoline engines. Even though the technology has been successfully implemented for more than 5 decades for internal combustion engines, maintaining the quality of the catalyst, developing engine compatible solutions with respect to continuously tighter emission regulations remains a big challenge. The combination of bi- (PtRh / PdRh) or tri-metallic (PtPdRh) formulations/solutions along with an appropriate Oxygen Storage Component (OSC) result in the formulation of successful TWC catalyst [1-2]. Rh is an important component of the TWC as it helps in reduction of NOx. In spite of these evident advantages some major challenges with regard to TWCs are still open: (i) Broadening of the operating air/fuel window (ii) Promoting the intrinsic activity by increasing the efficiency of TWCs by making them more cost efficient. (iii) using an alternative formulation by minimizing the use of rare and expensive Rh with very volatile costs [3].

Methodology & Results

Considering Rh prices increased significantly (Rh prices ranging from 379€/g to 860€/g in 2021, and currently again falling to 410€/g 2023) in previous years we developed a TWC composition containing only Ru and Ru with dopants (Ru: 17€/g – Jan 2023).



Comparison of Catalytic Activity under Fresh and Aged Conditions

The developed Ru catalyst compositions show the same and even better performance than current PtRh 1/1 or PtRh 5/1 TWCs under rich conditions. An cost effective Ru based TWC has been developed which can be effectively used under rich engine conditions.

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Noble metal catalysts for plasma-assisted oxidation of methane

J. Palo[1], J.Kihlman[1]

[1]*VTT Technical Research Centre of Finland, Espoo, Finland*
[*]*jasmiina.palo@vtt.fi*

Keywords: methane oxidation, non-thermal plasma, emission reduction, Pd, NH4-ZSM-5

Introduction. Dairy and meat production are accountable for around 150 Mt CO_2 equivalent of methane emissions every year in Europe [1]. These scattered, point-source emissions are found e.g., in cowsheds in ultra-low concentrations (50 – 200 ppmv). Currently there is no feasible technology to abate them, but the new EU regulations in Fit for 55 legislation package [2] will set target of reaching carbon neutrality for agricultural sector by 2035. Horizon Europe funded project CANMILK focuses on developing a combined process based on adsorption, catalysis and non-thermal plasma technologies to mitigate enteric methane emissions by converting CH_4 to less harmful CO_2.

Catalytic oxidation of methane to CO_2 is a mature technology used to convert dilute methane emitted during coal mines' venting and from vehicle exhaust [3]. In thermal processes, complete methane oxidation can be achieved at temperatures of 400 °C, and the reaction is typically catalyzed by noble metals such as Pd or Pt [3,4]. However, plasma technologies have potential to reduce environmental pollutants at ambient conditions and utilize renewable electricity for operation. A limited number of publications exist where plasma-assisted CH_4 oxidation is studied, especially for ultra-low methane concentrations.

Experimental. Non-thermal plasma or cold plasma is electrically charged matter in its gaseous form and can be generated by passing gases through an electric field [5]. However, plasma itself is non-selective. To counter the effect, a catalyst can be introduced into the reactor to improve product selectivity and conversion. These experiments were carried out by feeding simulated cowshed air to a dielectric barrier discharge (DBD) reactor, having a structure that enables the study of a catalyst within the plasma zone.

Results and discussion. The scope of this work was to study Pd catalysts supported on Al_2O_3 and NH_4-ZSM-5. The catalysts were synthesized for the experiments and compared for their activity to CH_4 oxidation reaction under similar operating conditions. The effect of material choice on system performance was further studied by means of applied power and gas hourly space velocity. As N_2 molecules can break down to N* radicals and further react with available O atoms to form nitric oxides, the formation of NO_x compounds was monitored during experiments, along with the surface temperature of the DBD reactor caused by the exothermicity of oxidation reactions. The effect of plasma on the studied catalyst was systematically evaluated using several characterization methods, including XRD, ICP, N_2 physisorption, and H_2 chemisorption.

Acknowledgments



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Na cation effect in zeolite on Direct Air Capture of CO_2

Do Yeong Kim[1], Wo Bin Bae[1], Sungjoon Kweon[2], Min Bum Park[2], Sung Bong Kang[1,*]

[1] *School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology, 123 Cheomdan-Gwagiro, Gwangju, 61005, Republic of Korea*

[2] *Department of Energy and Chemical Engineering, Incheon National University, 119 Academy-ro, Incheon 22012, Republic of Korea*

**sbkang@gist.ac.kr*

Keywords: Na cation, Zeolite, Direct Air Capture

Introduction.

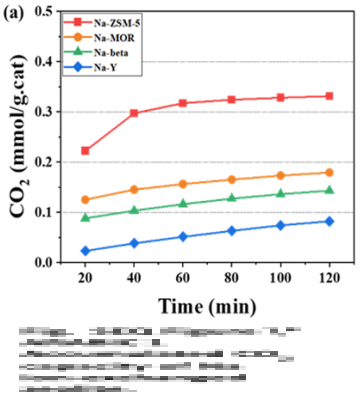
An increase in global temperature due to the greenhouse effect of carbon dioxide is an unavoidable fact. As part of efforts to reduce CO_2, direct air capture (DAC) technology removing CO_2 from ambient air using an efficient adsorbent at room temperature has been developing. A useful strategy for enhancing DAC performance is the chemical functionalization of zeolites such as an active cation into zeolite via ion exchange [1]. This work has investigated DAC performance with respect to the zeolite structure (beta, ZSM-5, mordenite, and Y). To determine the critical factor influencing CO_2 trapping and desorption behavior, analyses of the impacts of Na cation exchange in zeolites also have been done.

Experimental/methodology.

Four types of zeolites such as beta , ZSM-5 and Y zeolites provided from Zeolyst, and mordenite from Albemarle were characterized of the DAC performance. Na-form zeolite was synthesized by ion-exchange Na into NH_4-form zeolites using 0.8 M NaCl aqueous solution. The CO_2 adsorption breakthrough curves were observed with 400 ppm CO_2 and He balances at 25 °C. The desorption profiles were acquired by purging and ramping the temperature from 25 to 300 °C, respectively, in order to determine the physiosorbed and chemisorbed CO_2 on zeolites. The in-situ surface behavior of CO_2 adsorption on Na-exchanged zeolites was analyzed using DRIFT spectra, and the IR spectra of CO_2 desorption were also collected as a function of temperature (25, 70, 150, and 250 °C). NH_3-TPD and pyridine-IR were used to determine the characteristics and amounts of acidic sites.

Results and discussion.

In figure 1, the Na-ZSM-5 showed the maximum capacity of CO_2 with 0.33 mmol g^{-1} at room temperature and faster kinetics reaching breakthrough in less than an hour. For the chemisorbed CO_2 species, the Na-ZSM-5 had a distinctive desorption behavior, exhibiting two desorption peaks at different ramp temperatures, 65 and 260 °C, respectively. The doublet desorption peaks at relatively lower and higher temperatures provide evidence for two Na cation adsorption sites, Na I and Na II, respectively, in the ZSM-5 framework [2].



The behavior of CO_2 species on Na-zeolite adsorption sites was examined using in-situ DIRFTs to study surface adsorption. Unlike other zeolites, the Na-ZSM-5 showed a distinct CO_2 adsorption peak at 1638 cm^{-1}, which can be explained by the formation of carbonate species on the basic site of an Al-O group [3]. Furthermore, the complete desorption of CO_2 at 150 °C demonstrates how strongly the gas is absorbed as carbonate. A strong interaction between CO_2 and the basic site of zeolitic oxygen is critical for the capture of CO_2 chemisorbed over the Na-ZSM-5. The basicity of zeolitic oxygen (acido-basic site) could be caused by the strong Lewis acidity of the Na cation exchanged. According to the results of NH_3-TPD and pyridine-IR, the Na-ZSM-5 has stronger Lewis acid sites than Na-beta, -MOR, and -Y, showing that the ZSM-5 utilizes Na cation more effectively in the frameworks.

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Performance of Ni-Mn and Ni-Co-Mn mixed oxide catalysts in total oxidation of volatile organic compounds

T. Babii[1], K. Jirátová[2], J. Balabánová[2], M. Koštejn[2], J. Maixner[1], F. Kovanda[1*]

[1]*University of Chemistry and Technology, Prague, Czech Republic*
[2]*Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, Prague, Czech Republic*
[*]*Frantisek.Kovanda@vscht.cz*

Keywords: Ni-Co-Mn oxides, mixed oxide catalysts, VOC total oxidation

Introduction. Volatile organic compounds (VOC) can be removed from air by catalytic total oxidation to carbon dioxide and water as end products. Transition metal oxides are often used as catalysts in this process. The combination of multiple transition metal cations in these catalysts may increase their activity in VOC oxidation due to a possible synergistic effect. Recently we observed an enhanced catalytic performance of Co-Mn mixed oxides in the deep ethanol oxidation compared to Co and Mn oxides alone [1], whereas activity of the Ni-Co oxides decreased with increasing Ni content in the catalysts [2]. To investigate the activity of other types of oxides, we prepared Ni-Mn and Ni-Co-Mn catalysts by heating coprecipitated precursors and examined the effect of metal cations molar ratio in the catalysts on their physical chemical properties and catalytic performance in the VOC total oxidation.

Experimental/methodology. The oxide catalysts were obtained by heating of precursors, prepared by coprecipitation of nitrate solutions containing Ni, Co, and Mn in various molar ratios; the aqueous solution containing NaOH and Na_2CO_3 was used as precipitation agent. The washed and dried products were calcined for 4 h at 500 °C in air. The prepared catalysts were characterized by various methods (powder XRD, Raman spectroscopy, N_2 adsorption, H_2-TPR) and tested in the deep oxidation of ethanol and toluene, which were used as model VOC. The catalytic reaction was carried out in a fixed bed reactor with the inlet concentration in air of 750 (ethanol) and 780 ppm (toluene) at GHSV of 20 l g_{cat}^{-1} h^{-1}, using a tempereture ramp of 2.0 °C min^{-1}. The T_{50} and $T_{90}(CO_2)$ temperatures required to achieve 50% conversion of ethanol or toluene and 90% conversion of all organic compounds to CO_2 were chosen as a measure of catalyst activity.

Results and discussion. The Ni-Mn catalysts contained Ni-Mn mixed oxides (Ni_6MnO_8 and $NiMnO_3$ with murdochite and ilmenite structure). Powder XRD patterns of the Ni-Co-Mn catalysts showed mixed oxides with spinel structure, together with $(Ni,Co)MnO_3$ in the sample with high Mn content and NiO in the samples with high Ni content. Slight changes in spinel lattice parameter in dependence on the samples composition and broadening of the peaks in Raman spectra indicated a disordered distribution of cations in the spinel structure. In the ethanol oxidation, the Ni-Mn catalysts with Ni:Mn molar ratio of 1:1 showed the lowest T_{50} and $T_{90}(CO_2)$ temperatures (91 and 172 °C, respectively), indicating high activity of this catalyst. Similar T_{50} and $T_{90}(CO_2)$ temperatures were observed also for the Ni-Co-Mn oxide catalysts with lower Ni content. These catalysts showed also very good activity in the toluene oxidation with T_{50} temperatures around 230-235 °C. Surface area of the oxides had only minor effect on their catalytic performance. Acetaldehyde and carbon monoxide were detected as the main by-products of ethanol oxidation on the investigated catalysts. The mixed oxide catalysts with molar ratios of Ni:Mn and Ni:Co:Mn of 1:1 and 1:1:1 showed the highest activity and good selectivity in the deep ethanol oxidation among the prepared Ni-Mn and Ni-Co-Mn oxide catalysts. The presence of Co in the ternary Ni-Co-Mn catalysts did not have a significant effect on the catalytic activity compared to Ni-Mn catalyst with Ni:Mn molar ratio of 1:1 but impaired the selectivity of catalysts, specifically, increased formation of carbon monoxide was observed.

Acknowledgments
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Investigating of metal vanadate based catalysts in expediting NOx reduction at ultra-low temperatures and their applications

D.W. Kwon*, H.P. Ha

Korea Institute of Science and Technology, Seoul, South Korea
**Corresponding Author's E-mail address*
dwkwon@kist.re.kr

Keywords: NH_3-SCR, NOx reduction, metal vanadates, SO_2 resistance

Introduction.

Inventing a catalytic solid with high activity and selectivity to reduce NOx by NH_3 to form N_2 and H_2O (NH_3-SCR) at ultra-low temperatures is recently sought after to attenuate the atmospheric concentration of NOx, leading to mitigate severe air pollution.

Experimental/methodology.

V_2O_5 has been modified through the incorporation of secondary metal species to synthesize catalysts that outperform commercial catalysts for NH_3-SCR. It is the formation of a novel and interesting class of bimetallic V oxides such as $MeVO_4$. The NH_3-SCR performance was experimented in a fixed bed reactor (including Lab. and pilot scales).

Results and discussion.

The influence of metal vanadate catalyst on its activity and durability in the SCR (selective catalytic reduction) of NOx by NH_3 was investigated. The addition of Me-Sb adjusted the surface species composition and increased the number of Brønsted acid sites. The redox properties, number of surface oxygen vacancies, and amount of active labile oxygen were enhanced by the presence of metal vanadates. This species contributed to the improved moisture/sulfur resistance by causing sufficiently enhanced surface acidity and reduced SO_2 adsorption. In the NO rich condition, active oxygen and oxygen vacancies improved performance by achieving an optimal Me/V ratio. In contrast, in the NO_2 rich condition, the NOx reduction rate increased with the decrease in activation energy from the increase in Me/V ratio. The catalysts synthesized according to the Me/V ratio resulted in changes in the reaction rate and the type of adsorbed species. In this presentation, we highlight our recent pilot studies of the metal vanadate catalysts to diagnose its practical applicability as a NH_3-SCR unit. The metal vanadates catalyst is mass-produced, engineered to be a honeycomb monolith-typed catalyst bed, and installed in several NH_3-SCR units used for the stationery NOx-emitting sources (pilot test of combined cycle power plant). Our pilot studies corroborate that in comparison with a commercial catalyst, the metal vanadates catalyst reveals greater NOx conversions and superior resistance to poisons including SO_2 and ammonium (bi) sulfate. Furthermore, the metal vanadates catalyst, can provide outstanding long-term stability to catalyze NH_3-SCR at ultra-low temperatures. This is evidenced by the enhanced performance of the metal vanadate catalyst in real exhaust gas streams at 180 °C or lower temperature.

Acknowledgments

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Effect of different reductants on the NO SCR over Ag catalysts

Eleonora La Greca[1*], Tamara S. Kharlamova[2], Maria V. Grabchenko[2], Luca Consentino[1], Daria Yu. Savenko[2], Giuseppe Pantaleo[1], Olga V. Vodyankina[2] and Leonarda Francesca Liotta[1]

[a]*Institute for the Study of Nanostructured Materials (ISMN), (Italian) National Research Council (CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy*
[b]*Tomsk State University, Lenin Ave. 36, 634050 Tomsk, Russian Federation*
[*]*eleonora.lagreca@ismn.cnr.it*

Keywords: Lean NO_x reduction, HC-SCR reaction, Ag catalysts

Introduction.
Nitrogen oxides (NO, NO_2 and N_2O) derived from transport and power plants, are a major source of air pollution which contributes significantly to the formation of photochemical smog, acid rain and eutrophication, as well as being directly harmful to human health [1]. Among the various strategies used to remove these pollutants, a potential method is the selective catalytic reduction of NO (SCR) that showed excellent performance in reducing NO_x emissions from the diesel engine. Hydrocarbons (HC) / oxygenated hydrocarbons, unburnt alcohols (HCO) could be used as reducing agent in SCR reaction, simplifying the plant, reducing costs and making this process of particular interest [2], [3]. In this study the role of ethanol (C_2H_5OH) and propene (C_3H_6), as reducing agents in the NO-SCR over Ag catalysts deposited on CeO_2, MnO_2 and a $CeMnO_x$ mixed oxide, was investigated.

Experimental/methodology.
All the oxides, CeO_2, MnO_2 and $CeMnO_x$ (with molar ratio Ce/Mn = 1) were synthesized with the sol-gel method, using citric acid as a chelating agent (citrate method). The supports thus obtained were impregnated with aqueous solutions of $[Ag(NH_3)_2]\cdot NO_3$, in order to obtain catalysts with Ag loads of 1% by weight. The calcination of the oxides was carried out at 500 °C for 3 hours, while the catalysts with Ag were calcined in air at 500 °C for 2 hours. To estimate the activity of NO SCR and the effects of the different hydrocarbons, catalytic tests were performed using propene and ethanol. In the case of C_3H_6-SCR test, the mixture was composed of 1000 ppm in NO, 3600 ppm C_3H_6, 10 %vol in O_2, 2.9 %vol H_2 and He as balance gas; while EtOH-SCR tests were conducted using a reaction mixture composed of 1000 ppm of NO, 2 %vol of C_2H_5OH and 10 %vol of O_2 in He. The physiochemical properties of the catalysts were obtained by several characterization techniques, such as XRD, H_2–TPR, N_2-physisorption and Raman spectroscopy.

Results and discussion.
The NO SCR activity of Ag catalysts in presence of C_2H_5OH and C_3H_6 strongly depends on the nature of the reducing agent, but also on the support composition and as well on the oxidation state and particle size of silver. Catalysts with uniformly distributed Ag^+ and/or $Ag_n^{\delta+}$ species are the most active in the NO-SCR reaction, while the metallic clusters of Ag_n^0 are responsible for the non-selective oxidation of ethanol and propene.

Acknowledgments
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The use of Spaci-MS to spatio-temporally resolve Three-Way Catalysts

A. Lanza*, S. Raphy, L. Phillipson, A. Kolpin, D. Bounechada, A.P.E. York

Johnson Matthey Technology Centre, Sonning Common, United Kingdon

*aldo.lanza@matthey.com

Keywords: Spatially resolved capillary inlet Mass Spectrometry, Oxygen storage catalyst material, Three-way Catalyst, Automotive, Emission Control

Introduction. Spatially Resolved Capillary Inlet Mass Spectrometry (SPACI-MS, Figure 1a) [1,2] is a technique which allow to measure gaseous concentration and temperature along the axial profile of a structured catalyst's channel (figure 1b). The gas concentration is sampled through a capillary and analysed by a Mass Spectrometer. Three Way Catalyst (TWC) is the aftertreatment technology used to control emissions from Gasoline engines under a several air-to fuel ratios (rich/lean). Active sites are typically made by Platinum group metals, while supports as $Ce_xZr_{1-x}O_2$ play the role to store and provide oxygen when this is not available in the gas phase: lack of O_2 favours NO removal to N_2, but can also lead to undesired secondary emissions as NH_3 and N_2O (greenhouse gases). In this work, effect of the Oxygen Storage Catalyst material (OSC) was investigated by measuring the stored oxygen and the secondary emissions along the catalyst coordinate using SPACI-MS.

Experimental/methodology. Two JM TWC cores (OD = 1", L = 4.5", 600 CPSI) with and without Ce-based mixed oxide (with and without OSC) were tested under Lean to Rich cycles (30 s each). Feed composition of CO=0/2%, O_2=1/0%, NO=0-2000 ppm, H_2O =6%, carrier Ar (tot flow= 30 L/min), T=450-650°C. Gas phase composition and temperature were spatially (along the length of the channel) and temporally resolved with SPACI-MS (HIDEN®). An FTIR was used to check the outlet gas composition.

Results and discussion.

Figures 1a and 1b show the O_2 concentrations measured at each axial coordinate during the lean half cycle for both samples without NO (not reported for brevity). The gaseous O_2 is gradually stored along the catalyst channel, and the breakthrough of O_2 is delayed for the OSC core compared to the one without, thanks to the presence of the Ce oxide. The cumulative stored O_2 was reported in Figure 1c which shows less than half stored without the OSC material, if compared with the OSC core. NO was then co-fed on top of the original mixture to capture any change on the stored gaseous oxygen and NOx removal: NO partially stored [3] and oxidize to NO_2 during the the lean half cycle, while the remaining slips. When the CO oxidation front propagates by consuming the stored O_2 along the length, local rich conditions occur leading to H_2 and N_2O/ N_2/ NH_3 (Fig. 1d only NH_3 scan reported for brevity) via WGS reaction and NO reduction (and by stored NO_x surface species [3]), respectively. Within rich conditions the catalyst without OSC showed the highest NH_3 production due to the lower oxygen storage capacity which leads to higher H_2 production. In contrast, the OSC core showed the lowest NH_3 make since the H_2 was produced toward the rear of the core. In this work we demonstrated the capability to quantify oxygen storage and secondary emissions with a SPACI-MS during representative gasoline conditions. The catalyst with OSC showed the highest availability of stored oxygen along the whole channel, and the lowest NH_3 make as the higher oxygen storage capacity shifted the onset of rich conditions (therefore lower H_2 production from WGS) towards the rear of the core.

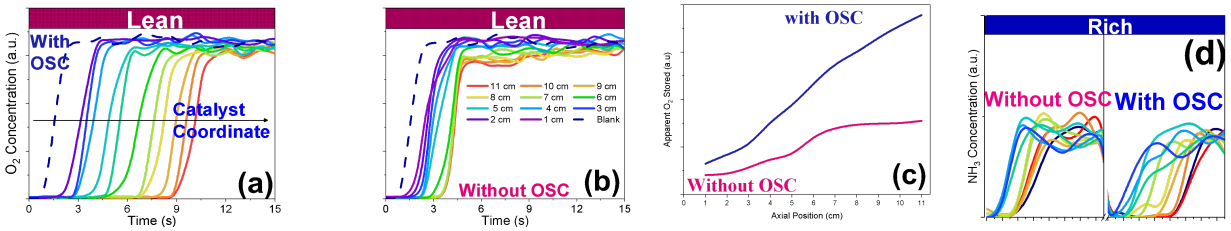

Figure 1. a.) Spatiotemporal profiles of O_2 (a) with OSC and (b) without OSC cores, NO=0 ppm, 600°C. (c) Overall O_2 stored. (d) NH_3 profiles

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Optimization of potassium glass composition for catalytic soot combustion by transition metal doping

P. Legutko[1*], E. Jarosz[1], M. Dziadek[2], G. Grzybek[1], M. Marzec[3], M. Michalik[4], A. Adamski[1]

[1]*Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Krakow, Poland*
[2]*WIMiC, AGH University of Science and Technology, Mickiewicza Ave. 30, 30-059 Krakow, Poland*
[3]*ACMiN, AGH University of Science and Technology, Mickiewicza Ave. 30, 30-059 Krakow, Poland*
4Institute of Geological Sciences, Jagiellonian University, Gronostajowa 3a, 30-387 Krakow, Poland
[*]*piotr.legutko@uj.edu.pl*

Introduction. Such particulates like soot, road dust or ashes suspended in the air show many adverse features, including those leading sometimes to various respiratory and circulatory diseases or, in unfavorable scenarios, to cancerous mutagenic changes. The use of alkali and transition metals can be considered as the most promising alternative to noble metals as catalytic components for soot combustion. Due to their relatively high desorption ability from oxide surfaces, alkali metals have to be intentionally stabilized within bulk matrices. Interesting results in this regard were obtained among others for such alkali-immobilizing matrices as glassy phases. There is however a lack of more systematic studies on doping of such alkali glass-based systems with transition metals (TMs) of pronounced redox properties, playing a role of active sites in many oxidation catalytic reactions. This work aimed to elucidate how doping of alkali glasses with such TMs as Mn, Fe, Co, Cu, Ni, and Ce can influence their properties in catalytic soot combustion.

Experimental/methodology. Potassium-silicate glass ($25K_2O$-$59SiO_2$-16CaO mol%) was synthesized from SiO_2, K_2CO_3, and $CaCO_3$ by simultaneous melting of this mixture at 1345°C for 1h. The doped glasses (containing 5 mol.% of individual dopant) were prepared by a consecutive melting of the parent system with a proper amount of TM (Mn, Fe, Co, Cu, Ni, Ce) oxide at 1340°C for 0.5h. Typical of glasses, the amorphous structure of the synthesized samples, was confirmed by XRD, RS and FTIR, their chemical composition by XRF, and surface properties were investigated by XPS, DRIFT and UV/Vis-DR. The activity of the synthesized samples was determined for both tight and loose contacts in the atmosphere intentionally enriched with NO and without this additive.

Results and discussion. Characterization techniques confirmed the amorphous character of the investigated samples typical of glass structures. The activity in soot combustion of all catalysts was high, however, the presence of Cu and Co additives led to an increase in activity in comparison to an undoped glass, while the remaining dopants did not influence or even decreased catalyst activity in soot combustion. A correlation between thermal potassium stability and catalytic activity was found (Fig. 1): the presence of stable surface potassium species resulted in a higher reactivity in soot combustion. This observation confirmed the theory of active carbonate species on the surface of alkali glasses.

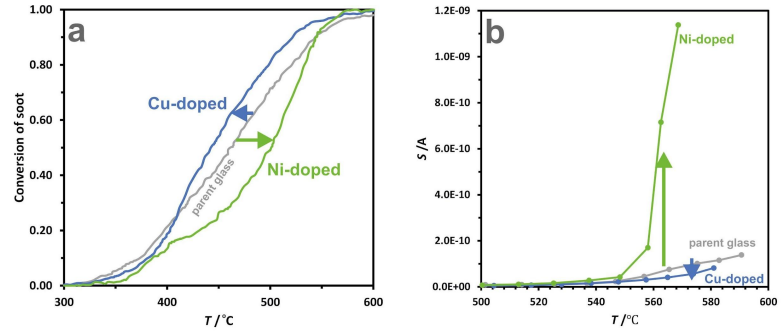

Fig. 1. Conversion of soot on Ni-, Cu-doped and undoped glass catalyst as a function of temperature (a) and thermal potassium desorption flux from those surfaces (b).

Acknowledgments

This work has been supported from the Anthropocene Priority Research Area budget under the program "Excellence Initiative – Research University" at the Jagiellonian University

Excellent hydrocarbon tolerance of CeO_2-WO_3-SnO_2 oxide catalyst for the NH_3-SCR of NOx

Jingjing Liu[1‡], Xiaoyan Shi[1,3‡], Yunbo Yu[1,2,3], Qingcai Feng[1], Hong He[1,2,3]*

[1] *State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China*

[2] *Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China*

[3] *University of Chinese Academy of Sciences, Beijing 100049, China*

‡*These authors contributed equally.*

*honghe@rcees.ac.cn

Keywords: CeO_2-WO_3-SnO_2, NH_3-SCR, Hydrocarbon resistance, HCN emission, Ammoxidation

Introduction. The tolerance of NH_3-SCR catalysts towards hydrocarbon compounds (HCs) is very important for their practical application on diesel vehicles. Recently we developed a Ce-W-Sn composite oxide catalyst (hereafter referred to as $CeWSnO_x$) that exhibited fairly high effectiveness for NO_x reduction and superior hydrothermal stability.[1-2] Even after extreme hydrothermal aging treatment at 1000 °C for 3 h, this catalyst still showed >90 % NO_x conversion at 300-550 °C. To further evaluate the possibility of practical application of this catalyst for diesel emission control, the effects of hydrocarbons on the NH_3-SCR activity of the $CeWSnO_x$ catalyst were systematically investigated in this work. For comparison purposes, the commercially available NH_3-SCR catalyst, namely Cu-SSZ-13, was also examined under the same conditions.

Experimental/methodology. The $CeWSnO_x$ catalyst with Ce: W: Sn molar ratio of 1: 0.24: 2 was prepared by a coprecipitation method using ammonium hydroxide as the precipitant. The catalytic activity tests were carried out in a quartz tube plug flow reactor. The simulated reaction gases consisted of 530 ppm NH_3, 500 ppm NO, 5 vol. % O_2, 5 vol. % H_2O and balance N_2 with 859 ppm of propene.

Results and discussion. Experimental results[3] suggested that the $CeWSnO_x$ showed much better HC tolerance than the Cu-SSZ-13 (**Figure 1**). This property mainly originated from the strong HC oxidation capacity of the $CeWSnO_x$ due to Sn introduction, which significantly inhibited side reactions, including the HC ammoxidation and the carbon deposition reactions. In contrast, an undesired HC ammoxidation reaction occurred at medium temperatures over the Cu-SSZ-13 in the presence of propene, accompanied by the emission of toxic HCN gas. The high HC tolerance of $CeWSnO_x$ gives it promise for application on heavy-duty diesel after-treatment systems in the future, especially those with the SCR-on-DPF or cc-SCR configuration.

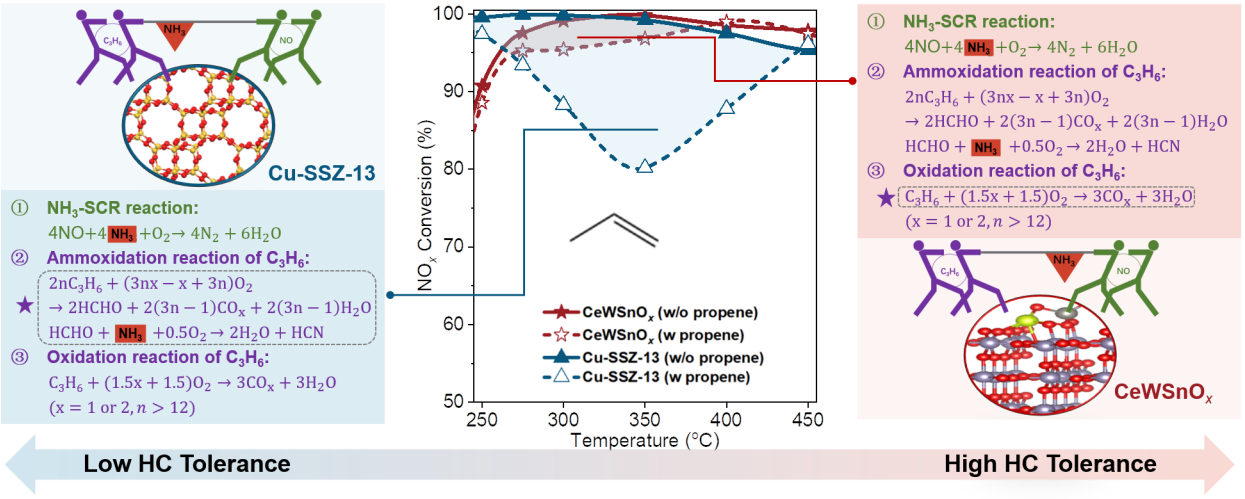

Figure 1. The effects of propene on the NH_3-SCR performance of $CeWSnO_x$ and Cu-SSZ-13 catalysts.

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Small Gas Molecule CO *in situ* Directed Highly Stable In-Plane 1T phase Boost Co-MoS_2 Thiophene Hydrodesulfurization

Lei Liu, Ning Liu, Biaohua Chen*
Faculty of Enviroment and Life, Beijing, China (100124)
* chenbh@bjut.edu.cn

Keywords: 1T phase transition, CO structure directing agent, hydrodesulfurization, basal plane activation

Introduction. MoS_2 is a typical hydrodesulfurization (HDS) catalyst [1], which has also been widely applied in the electronic devices, optoelectronics and energy storage. Considering the basal plane covering huge area of MoS_2, however, being inert for the reactions, great attentions have been recently concentrated on the basal plane activation to promote MoS_2 activity. The 2H⟶1T phase transition can efficiently activate the basal plane of MoS_2 [2], which however greatly suffers from the low thermostability of the transformed 1T phase. In this regard, developing a simple 2H⟶1T phase transition method to form stable in-plane 1T phase sites is highly desirable to activate the basal plane of MoS_2.

Experimental/methodology. A series of Co-MoS_2-n (n=0, 0.3, 1.0 and 2.0, representing CO pressure) was synthesized by hydrothermal synthesis approach with *in situ* introducing CO into the system. The XRD, Raman, XPS, EPR, HRTEM, Cs-corrected TEM and EXAFS were employed to characterize synthesized samples and the density functional theory (DFT) and ab initio molecular dynamic (AIMD) were employed to shed deeper insight into the effect of CO during 2H⟶1T phase transition.

Results and discussion.

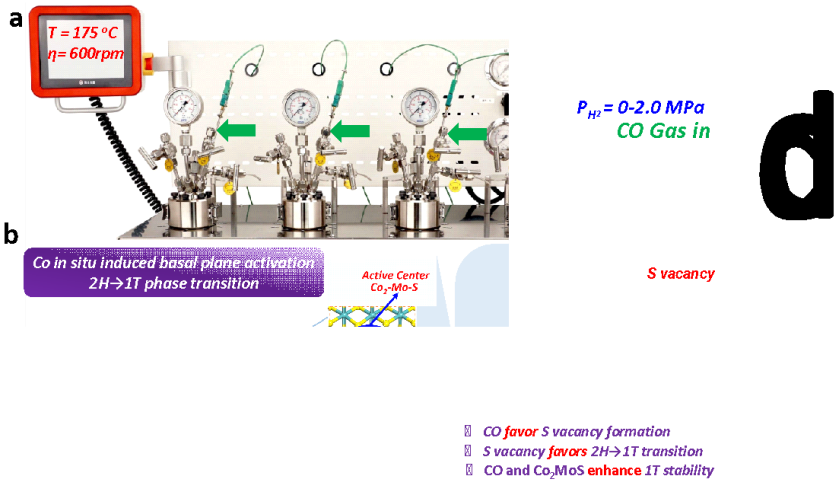

Fig. 1 Schematic illustration of CO assisted one-step synthesis of Co-MoS_2-n and thiophene HDS activity measurement.

Present work utilzing CO as the SDA successfully syntheiaze one type of Co-MoS_2-0.3 with high ratio of thermostalbey 1T pahse (70.6%, after 350 °C annealing). The realted thiophene HDS activity (see Fig. 1c) surpasses most of recently reported MoS_2-based catalysts. The the kinetics and thermodynamics effects of CO on 2H⟶1T phase transition were well illustrated based on the combined experimental and theoretical studies. A basic atomic structure of "Co_2-Mo-S" (in-plane S being coordinated by two Co and one Mo) was identified based on the EXAFS (extended X-ray adsorption fine structure), Cs corrected TEM and DFT (density functional theory) calculation, which significantly favors the CO-directed 2H⟶1T phase transition and thiophene HDS. Present work has developed a simple phase-engineering approach to achieve high ratio of thermostable in-plane 1T phase, which would substantially favor other highly efficient MoS_2-based catalyst designs.

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Evaluating the uncatalysed and catalysed soot combustion behaviour from TG-MS analysis: a kinetic study

I. Mekki[1], I. García-Prieto[1], J. A. Caballero-Suárez[2], P. Piqueras[3], J. De la Morena[3], and A. García-García[1*]

[1]*MCMA Group, Department of Inorganic Chemistry and Institute of Materials, University of Alicante, Alicante, Spain*

[2]*Department of Chemical Engineering, University of Alicante, Alicante, Spain*

[3] *CMT-Motores Térmicos, Universitat Politècnica de València, València, Spain*

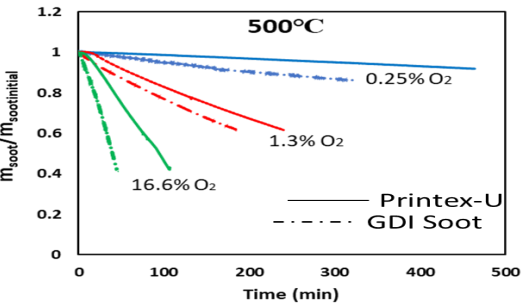
*a.garcia@ua.es

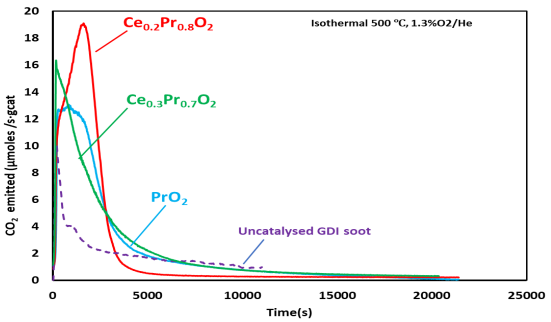
Keywords: model soot, GDI soot, soot combustion, praseodymia-based catalysts, kinetic study

Introduction. By 2020, the European Union has imposed a CO_2 emission target of 95 g/km for passenger cars. Gasoline Direct Injection (GDI) engines technology has the potential of substantially improving the overall fuel economy and thus, reducing CO_2 levels. One of the main disadvantages of GDI engines is the high emission of particles (mainly those of very low size) compared to conventional gasoline engines. Therefore, GPFs (Gasoline Particulate Filters) have been commercialized and are rapidly becoming a ubiquitous part of new GDI after-treatment systems [1]. In the present communication, the goal is to analyse the uncatalysed and catalysed combustion behaviour of model soot (Printex-U) and a GDI soot.

Experimental/methodology. For this study, Printex-U (model soot supplied by Evonik-Degussa) and a real GDI soot (supplied by CMT-UPV) were used to evaluate the uncatalysed soot oxidation characteristics. The soot (1 mg) was placed in a crucible in a TG-MS apparatus, by conducting isothermal tests at the temperature range of interest because of the application studied (500-525-550°C), combined with different O_2 concentrations (0.25-1.3-16.6%). These values emulate real working conditions of a GDI engine. Besides, soot combustion activity was evaluated by using a catalyst/soot weight ratio of 20/1 under *loose contact* mode. The selected catalysts (PrO_2, $Ce_{0.2}Pr_{0.8}O_2$, $Ce_{0.3}Pr_{0.7}O_2$) were prepared by the direct calcination of the cerium and praseodymium nitrate precursors for 1 hour at 500°C [1].

Results and discussion. The detailed analysis of the results suggests that whatever the conditions tested, GDI soot is more reactive than Printex-U, especially at low carbon conversions. For instance, Printex-U shows reaction order values around 0.45, independently on the oxygen concentration studied in this case. This differs slightly from those values expected for shirking core model (0.67) studied, which considers soot particles as non-porous spheres. The effect of the O_2 concentration on the soot oxidation was also analysed in terms of temporal evolution of m_c/m_{c0}. Soot





consumption rates clearly increase upon increasing the oxygen concentration, being more critical from 0.25% to 1.3% in O_2 (see Fig. 1). For the catalysed reaction, paying attention to the rate of CO_2 emission for GDI soot (Fig. 2), it is worth to note that very high rates of consumption are reached at the very beginning of the reaction (with nearly 100% of selectivity towards CO_2). The set of catalysts chosen are very promising for this demanding application, being $Ce_{0.2}Pr_{0.8}O_2$, which presents an interesting balance among textural and redox properties, the optimal composition found.

Figure. 1. Printex-U

Figure. 2. CO_2 emission profiles for the GDI catalysed as well as uncatalysed reaction

Effect of oxygen concentration on and GDI soot oxidation at 500°C

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Pd-Pt catalysts supported over Co modified alumina for the methane combustion and CO oxidation

Lazar Minkov[1*], An. Naydenov[2], Il. Hristova[1], H. Kolev[1], S. Todorova[1]

[1] Institute of Catalysis, Bulgarian Academy of Sciences, Sofia 1113, Acad. G. Bonchev str., bl.11, Bulgaria
[2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

Keywords: methane combustion; CO oxidation, Pd-Pt-Co catalysts

Introduction. Methane, a potent greenhouse gas, is recognized to contribute more to global atmosphere warming than carbon dioxide at equivalent emission rates. Moreover, methane is the hydrocarbon with the lowest reactivity and therefore the most difficult to be oxidized. Among noble metals, palladium is widely considered to be capable of guaranteeing high activity towards methane combustion. According to the literature date that modification of Pd with Pt results in catalysts with improved resilience with time on stream and increased catalytic activity in comparison to monometallic Pd catalysts. In our previous investigations we found that the addition of Co significantly improves the catalytic activity, and this depended on the sequence of cobalt and Pd introduction. That was the reason to direct our research to the system Pd−Pt−Co supported on Al_2O_3.

Experimental/methodology. The Al_2O_3 (SBET=225 m^2/g) was first impregnated with aqueous solution of $Co(NO_3)_2.6H_2O$ and calcined 2 h at 450 °C in air. After that the monometallic and bimetallic samples were prepared by impregnation of Co-Al_2O_3 or by successive impregnation with the corresponding salts or from a mixed solution. After each impregnation the catalysts were calcined 2 h at 450 °C in air. The as prepared catalysts were tested in CH_4 combustion and CO oxidation. Characterization techniques, X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD) and FTIR have been used to investigate the surface structure and bulk composition all catalysts.

Results and discussion. No palladium, palladium and cobalt phases were detected by XRD, revealing finely divided of Pd, Pt and cobalt particles. FTIR spectra of the fresh and worked Pd-Pt-Co catalysts show two wide bands one in the region 550-600 cm^{-1} and other in the interval 650–700 cm^{-1}. IR absorption at 670 cm^{-1} is ascribed to the vibrational bands of Co^{2+} in the $Co^{II}Al_2O_4$ spinel phase. The pink colour of the sample suggests that in this sample the Co ions have not undergone any oxidation process and they exist as Co^{2+} species in the octahedral sites.

Sample	S_{BET}, m^2/g
Pd+Pt/ Co-Al_2O_3	223
Pd+Pt/ Co-Al_2O_3-MS	236
Pt/Co- Al_2O_3	232
Pd+Pt/Co-Al_2O_3	227

Table 1. Samples characteristics

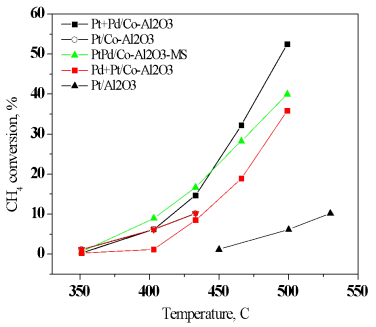

Figure 1. Conversion vs. temperature in the reaction of complete methane oxidation

H_2O and CO_2 were the only detectable reaction products on all studied samples in methane oxidation. The low activity in CO oxidation was observed for a tested catalyst. The improving in activity was observed for Pt catalysts modified with Co also. The additional increase in activity was seen after Pd addition. The row of activity in as follows: Pt-Pd> PdPt Ms > Pd-Pt>Pt.

Acknowledgments

This work was supported by the European Regional Development Fund within the OP "Science and Education for Smart Growth 2014 - 2020", Project CoE "National center for/of mechatronics and clean technologies ", №

Performance analysis of isostructural Cu-CHA-zeolites in NSR-SCR Hybrid DeNO$_x$ Technology for Diesel Engines

S. Molina-Ramírez[1*], M. Cortés-Reyes[1], C. Herrera[1], M.A. Larrubia[1], L.J. Alemany[1*]

[1]*Departamento de Ingeniería Química, Facultad de Ciencias, Universidad de Málaga, Málaga, España*
[*]*smolina@uma.es; luijo@uma.es*

Keywords: DeNO$_x$ hybrid technology, NSR-SCR, Cu-CHA-zeolites, SAPO-34, SSZ-13

Introduction.

Road-transpor sector is still the major air pollution contributor of harmful NO$_x$ emissions in Europe. The new Euro 7 regulation declared the importance of the development of DeNO$_x$ technologies, based on the combination of the current technologies and knowledge of all relevant pollutants control systems. Two catalytic technologies are widely used for this purpose are NO$_x$ Storage and Reduction (NSR) and Selective Catalytic Reduction (SCR) in diesel engines. The coupling between a NO$_x$-Trap followed by a NH$_3$-SCR catalyst leads to an improved N$_2$-selectivity, by the storage and reaction of the undesired NH$_3$ produced in the NSR catalyst in the downstream SCR system. This contribution is focused on the synthesis of two isostructural CHA-zeolites with Cu integrated in their structure, SAPO-34 and SSZ-13, and the combination and analysis of the behavior in NO$_x$ abatement activity in the NSR-SCR hybrid system.

Experimental/methodology.

For the NSR system, a model catalyst (Pt-Ba-K/Al_2O_3) was used [1]. As SCR catalysts, Cu-CHA-zeolites precursor gel phase was synthesized containing 2 wt.% of Cu by an ultrasound-assisted hydrothermal method and the calcined materials were identified as 2Cu-SAPO-34 and 2Cu-SSZ-13. Cu-zeolites were well-characterized. DeNO$_x$ activity of the NSR+SCR system was evaluated in a fixed-bed tubular reactor in isothermal and transient regime using a MultiGas MKS 2030 FTIR analyzer and the QMS200 Mass Spectrometer for online monitoring the outlet product distribution. Cyclic alternating lean (3%O_2) and rich (1%H_2) fuel conditions were used maintaining the concentration of NO (600 ppm), CO_2 (0.3%) and H_2O (1.5%) He-balanced, GHSV=30000h^{-1} and the T-range of 200-350ºC.

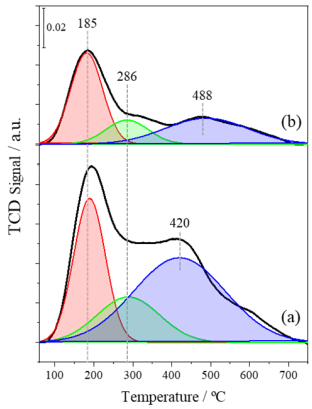

Figure 1. NH$_3$-TPD profiles for Cu-CHA-zeolites: (a)2Cu-SAPO-34 and (b) 2Cu-SSZ-13

Results and discussion.

Table 1. DeNO$_x$ activity results at 250 ºC

Configuration	X_{NO_x} (%)	S_{N_2} (%)	S_{NH_3} (%)	S_{N_2O} (%)
NSR	52.3	69.6	21.6	8.8
NSR+2Cu-SAPO-34	63.7	89.4	0.02	9.6
NSR+2Cu-SSZ-13	58.8	94.1	0.00	5.8

In NH$_3$-TPD profiles (Fig. 1) a low-temperature (185ºC) signal related to Brønsted acid sites was observed, a medium-temperature signal (286ºC) due to NH$_3$-adsorbed on strong Lewis acidic sites, associated with

isolated Cu^{2+} sites, was identified for both Cu-zeolites but more evident for Cu-SAPO-34. The existence of different Cu-species (confirmed by FTIR analysis with probe molecules) causes the shift to the T-max desorption signal of the Brønsted sites and influences the deNO_x activity. NO_x conversion and selectivity values (Table 1) indicated an enhancement of NO_x removal capacity for both hybrid systems compared to the single bed, due to the NH_3-SCR reaction. 2Cu-SSZ-13 catalyst presented a lower acidity and a lower Cu^{2+} ion population that, in spite of not being as active in NO conversion, is able to inhibit the occurrence of parallel reactions with N_2O formation, increasing nitrogen selectivity, with values around 94%, which makes this catalyst more suitable for its use in the hybrid catalytic system.

Acknowledgments

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Micro-/Mesoporous Cu-Containing Zeolites Investigated in NH_3-SCR-DeNO$_x$

A. Mollá Robles[1], M. Fernadi Lukman[2], A. Pöppl[2], R. Gläser[1], M. Jabłońska[1*]

[1]*Institute of Chemical Technology, Universität Leipzig, Leipzig, Germany*
[2] *Felix Bloch Institute for Solid State Physics, Universität Leipzig, Leipzig, Germany*
[*]*magdalena.jablonska@uni-leipzig.de*

Keywords: NH_3-SCR-DeNO$_x$, SSZ-13, ERI, copper.

Introduction. The selective catalytic reduction of nitrogen oxides by ammonia (NH_3-SCR-DeNO$_x$) is the most used emission control process for both stationary and mobile sources of NO$_x$. Copper-containing catalysts have been broadly investigated in NH_3-SCR-DeNO$_x$, while some reports claim an increase in NO conversion over micro-/mesoporous Cu-containing ZSM-5 or SAPO-34 [1,2]. On the contrary, it has been claimed that the mesopores introduced into Cu-containing zeolites ZSM-5 or Y do not play any direct role in the activity on NH_3-SCR-DeNO$_x$ [3,4]. Thus, further research is needed to explore these contradictions.

Experimental/methodology. SSZ-13 and ERI (obtained from Clariant) were subjected to post-synthetic treatments with an acidic and/or an alkali solution, followed by filtration and washing until neutral pH. Afterward, they were ion-exchanged with an aqueous NH_4NO_3 solution, calcined, and finally ion-exchanged with Cu(II) acetate. After pretreatment, the samples were investigated in the NH_3-SCR-DeNO$_x$ and thoroughly characterized with respect to their structure, composition, morphology (XRD, ICP-OES, SEM), texture (N_2 sorption), and redox properties, as well as the nature of their copper species (TPR-H_2, DR UV-Vis, EPR).

Results and discussion. The comparison of Cu-containing zeolites with different topologies (ERI and SSZ-13, Fig. 1a) reveals that Cu-SSZ-13 exhibits a significantly higher NO conversion than the other catalysts. The post-synthetic modification of the investigated zeolites influences the catalytic activity in different ways. Regarding the Cu-containing ERI, the NO conversion is higher for catalysts with modified supports (Fig. 1b). The NO conversion does not vary among different post-synthetic treatments, with either NaOH or HNO_3. For the Cu-containing SSZ-13 catalysts (with modified zeolites), a lower NO conversion in NH_3-SCR-DeNO$_x$ is observed. According to physico-chemical characterization, the modification of the supports results in the presence of different amounts and kinds of copper species (especially isolated Cu^{2+} and aggregated Cu species).

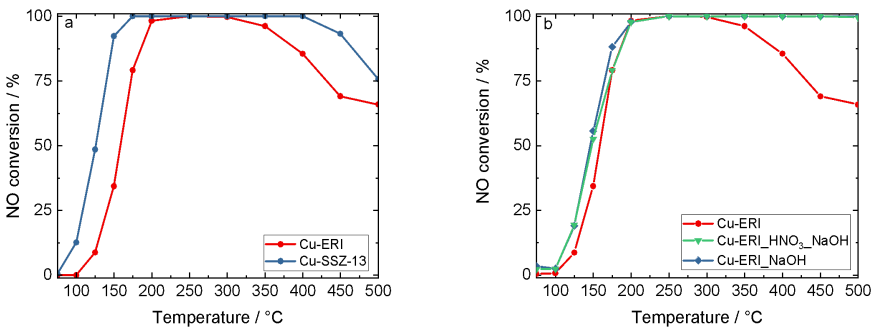

Figure 1. NO conversion over Cu-containing zeolites with different topologies (a) and different post-synthetic treatments of the support (b) studied in NH_3-SCR-DeNO$_x$.

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NH_3-SCR catalytic performance of natural clinoptilolite modified with hydrotalcite-like phase

A. Szymaszek-Wawryca[1*], P. Summa[1], U. Díaz[2], D. Duraczyńska[3], B. Samojeden[1], M. Motak[1]

[1]*Faculty of Energy and Fuels, AGH University of Science and Technology, Al. Adama Mickiewicza 30, 30-059 Krakow, Poland*
[2]*Instituto de Tecnología Química, UPV-CSIC, Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos, s/n, 46022 Valencia, Spain*
[3]*Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Ul. Niezapominajek 8, 30-239 Krakow, Poland*
[*]*Corresponding Author: agnszym@agh.edu.pl, motakm@agh.edu.pl*

Keywords: clinoptilolite, hydrotalcite, transition metals, $DeNO_x$

Introduction. Clinoptilolite, which belongs to the heulandite (HEU) family, is one of the most common natural zeolites and, due to its advantageous physicochemical properties, it has been used in many industrial processes [1]. It was proved [2] that iron-modified clinoptilolite exhibits very promising catalytic features as a support for NH_3-SCR catalysts. However, one of the challenges for the implementation of this material is to change its temperature window to the lower range. The problem can be solved by the deposition of a well-dispersed active phase in the form of mixed metal oxides, which contribute to low-temperature NO conversion. This goal can be reached by co-precipitation of hydrotalcite-like (HT) phase on the surface of clinoptilolite. The advantage of such modification is related to the fact that Mg^{2+} and Al^{3+} in HT building units can be substituted by catalytically active chemical elements, such as Cu^{2+} and Fe^{2+} [3]. Additionally, calcination of hydrotalcite-like materials yields mixed metal oxides, which could contribute to NO reduction in both the low- and high-temperature range. Therefore, the presented studies were focused on the synthesis, physicochemical characterization, and NH_3-SCR catalytic performance of clinoptilolite covered with hydrotalcite-like phase.

Experimental/methodology. Natural clinoptilolite was hydrogenated using HCl solution and modified with hydrotalcite by co-precipitation at constant pH. The HT phase contained Al^{3+} and Fe^{3+} (as trivalent metals, Me^{3+}) and Mg^{2+} and Cu^{2+} (as divalent metals, Me^{2+}) and the Me^{2+}/Me^{3+} molar ratio was 3:1. The amounts of metal precursors were adequately adjusted to obtain 20, 25, and 30 wt% coverage of the zeolite with HT phase. The physicochemical properties of the samples were determined using ICP-OES, low-temperature N_2 sorption, XRD, UV-Vis, TGA, FT-IR, and SEM, while the catalytic performance was investigated within 150-450 °C using a model gas mixture containing 800 ppm NO, 800 ppm NH_3, 3.5 vol.% O_2, and He as an inert.

Results and discussion. The obtained results showed that the NH_3-SCR catalytic performance of the materials was not related to the HT loading on the clinoptilolite. The deposition of the HT phase on the zeolitic support had a positive impact on NO conversion within 250-450 °C, which was related to the Brönsted acid sites present on the surface of clinoptilolite. UV-vis experiments on the spent catalysts indicated formation of Fe- and Cu-sites of higher nuclearity during the catalytic reaction. Hence, calcination prior to the catalytic reaction was not required for satisfactory NO conversion in the investigated temperature range.

Acknowledgements

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$VO_x/WO_3/TiO_2$ catalysts for NO_x abatement with NH_3-SCR: investigation of the role of tungsten

C. Nannuzzi[1*], L. Mino[1], S. Bordiga[1], M. Sist[2], J.M. Houghton[2], P.N.R. Vennestrøm, T.V.W. Janssens[2], G. Berlier[1]

[1]*Department of Chemistry, NIS and NISTM Centres, Università di Torino, via P. Giuria 7, 10125-Turin, Italy*
[2]*Umicore Denmark ApS, Kogle Allé 1, 2970 Hørsholm, Denmark*
[*]*chiara.nannuzzi@unito.it*

Introduction. Power plants, ships, and diesel engines are producing NO_x (NO and NO_2) during combustion processes in oxygen-rich conditions. The selective catalytic reduction by ammonia (NH_3-SCR) converts NO_x into N_2 and water, preventing the release of these compounds in the atmosphere, with related health and environmental concerns [1]. VO_x/TiO_2 based catalysts are the catalysts of choice in heavy-duty vehicles and large plants, usually promoted with Mo and/or W to improve thermal stability and activity. The role of promoters on the active sites could be chemical (modification of the electronic properties of VO_x) or physical (modification of VO_x dispersion by 'crowding'), as debated in the literature [2,3].

Experimental/methodology. A series of VO_x/TiO_2 with variable VO_x and two series of $VO_x/WO_3/TiO_2$ catalysts with fixed VO_x and variable WO_x content were prepared, tested in the title reaction and characterized by IR of CO probe molecules and Raman spectroscopies.

Results and discussion. Raman spectroscopy shows a good dispersion of V-O-V and V-O-W species in all catalysts. In both $VO_x/WO_3/TiO_2$ series, keeping constant the amount of V the activity increases with W up to 5 (V+W) atoms/nm^2 (Figure 1a), which would correspond to the monolayer according to IR spectra of adsorbed CO.

According to a widely accepted mechanism, the active V^{5+}=O site is reduced during the reaction to V^{4+} and rapidly oxidized again [3]. This would imply that in oligomeric V-O-V and V-O-W species, one V atom is the active redox site and the second one is helping in the reoxidation step. Following this hypothesis, the rate constant has been normalized to the theoretical amount of V active sites for each catalyst. Figure 1b shows higher values for W-free catalysts, suggesting a higher activity for V-O-V than V-O-W pairs. This points to the conclusion that the effect of W on the catalytic activity is to favor the formation of V-O-V species by crowding effect.

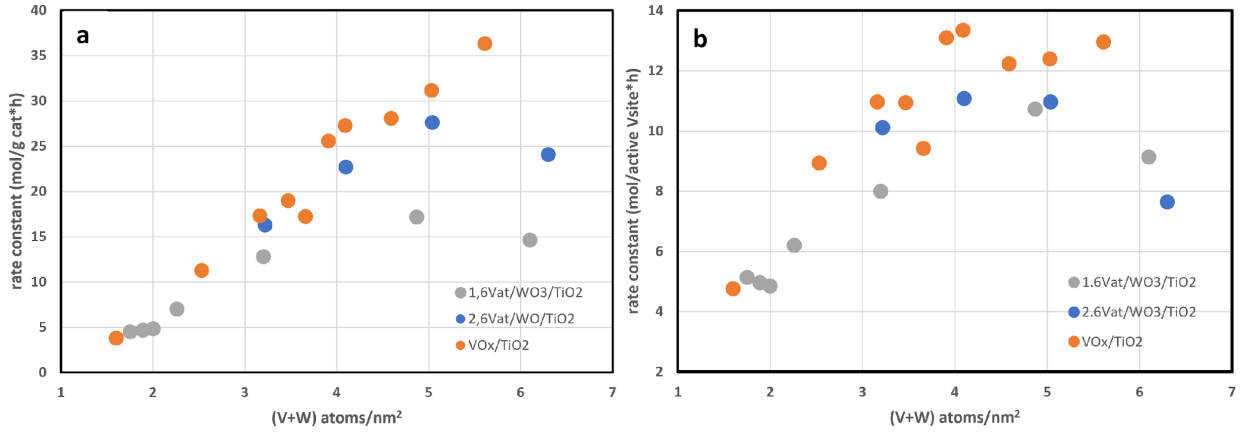

Figure 1. Rate constant at 250°C normalized to a) catalyst mass and b) theoretical amount of V active sites for two series of $VO_x/WO_3/TiO_2$ and VO_x/TiO_2 catalysts.

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Surface property studies on Sb promoted VO_x/TiO_2 NH_3-SCR catalysts

Alexander Nellessen[1,2], Andreas Schaefer[1,2], Anna Martinelli[1], Per-Anders Carlsson[1,2*]

Chalmers University of Technology, Department of Chemistry and Chemical Engineering
[1]*Division of Applied Chemistry and* [2]*Competence Center for Catalysis, SE-41296 Gothenburg, Sweden*
[*]*per-anders.carlsson@chalmers.se*

Keywords: in situ DRIFTS, NH_3-SCR, VO_x/TiO_2, Sb.

Introduction. Environmental protection and the legislative tightening of NO_x emissions in the mobile sector have provoked many efforts for the development of effective catalytic systems in the NH_3-SCR technology. Among these, titania supported V-based catalysts are commonly used, given to the low material costs and high resistance to sulfur compounds.[1] However, the catalyst has to work under dynamic conditions in a broad temperature window. Both low-temperature activity and stability at high temperatures are needed. The introduction of antimony on the catalysts have found to be an effective promoter to meet these requirements.[2] Our work is focused on surface properties studies on metal promoted VO_x/TiO_2 catalysts to understand the interaction of antimony with the TiO_2 support and vanadium.

Experimental/methodology. A series of Sb-promoted support and VO_x/TiO_2 catalyst was prepared via incipient wetness impregnation and additionaly thermally treated to mimic a long term use. The surface species and catalyst morphology were studied by in-situ infrared spectroscopy in diffuse reflectance mode (DRIFTS), Raman spectroscopy, NH_3-TPD, and surface BET area.

Results and discussion. The results from the NH_3-TPD show that the Sb-promoted TiO_2 support reveals a higher NH_3 adsorption capacity after the thermal treatment. In addition the adsorption capacity of the promoted catalyst is slightly decreased, indicating that antimony stabilizes both the support and the vanadium species.
The DRIFTS spectra of the Sb promoted support for the NH_3 adsorption at room temperature show that both promoted support and catalyst show a higher intensity for the negative OH bands after the thermal treatment. This can related to the formation of Sb-OH-Ti and V-OH-Sb groups that provide additional reaction sites in the SCR reaction. In the NH region, the higher intensity of the bands between 1483-1433 cm^{-1} indicates a higher amount of Brönsted acid sites by formation of Sb-OH-Ti.

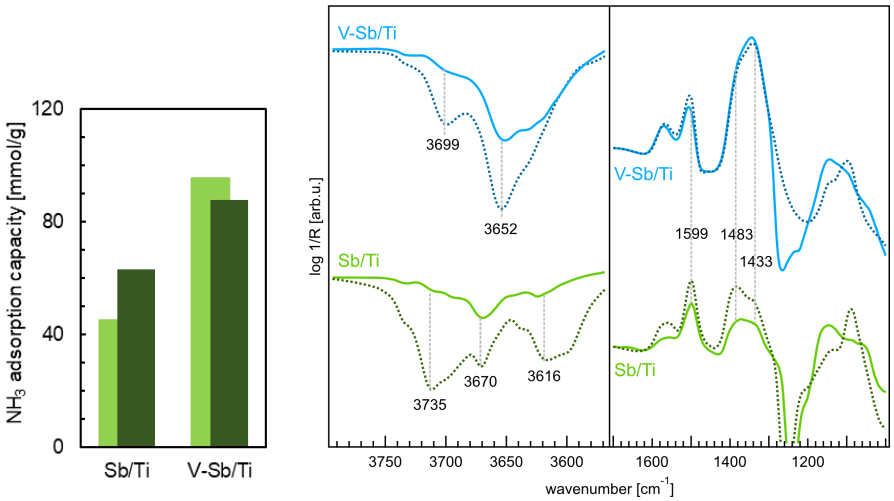

Figure 1: Integrated areas of NH_3-TPD profiles (a) and in situ DRIFTS spectra for the NH_3 adsorption at 25 °C of Sb promoted TiO_2 support and VO_x/TiO_2 catalyst before (solid line) and after thermal treatment (dashed line).

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Processing a burner gas from autothermal biogas combustion for syngas production

K. Neubauer[1], U. Armbruster[1], S. Wohlrab[1*], S. Anger[2], H.-P. Schmidt[3]

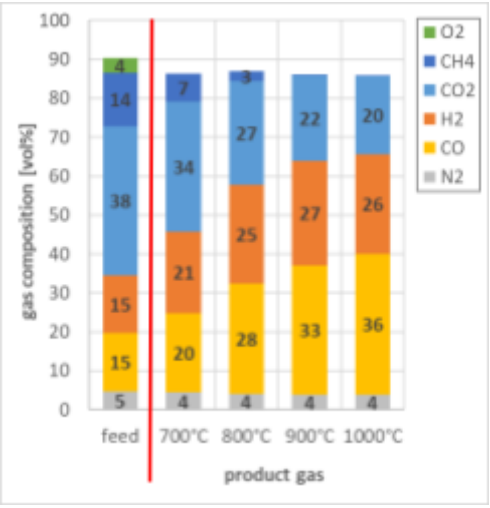
[1]*Leibniz Institute for Catalysis, Rostock, Germany*
[2]*DBI – Gastechnologisches Institut gGmbH Freiberg, Freiberg, Germany*
[3]*WS Reformer GmbH, Renningen, Germany*
[*]*sebastian.wohlrab@catalysis.de*

Keywords: syngas production from biogas, high-temperature catalyst, reforming

Introduction. Typically, biogas (mainly containing CH_4 and CO_2) is often used in low-value applications such as heating. In contrast, it can be converted into syngas by reforming to produce high-value liquid fuels or chemicals without the need for prior CO_2 capture [1]. This process is often called 'bi-reforming' or Steam Biogas Reforming (SBR), which combines steam and CO_2 reforming of methane [2].

Experimental/methodology. Using a simulated feed gas composition derived from modeling the effluent from autothermal combustion of biogas with O_2, the reforming activity of various catalysts was investigated in a laboratory facility with a 3-zone high-temperature furnace above 950 °C. The feed gas was composed of 5 pure gases (CH_4, CO, CO_2, H_2 and O_2) mixed with evaporated water. Measurement of the feed and product gas composition was done online via FID and TCD detection with N_2 as internal standard.

Results and discussion. An innovative process for the production of methanol from biogas using hydrogen and oxygen from renewable sources is being developed. The decisive step is the coupling of a new burner concept (ADROX-FLOX) with high-temperature catalysts for downstream gas conditioning towards syngas.



Catalysts with spinel or perovskite structure as well as metals supported on alumina were investigated. For example, Co-$AlLaO_x$ showed very good stability at high temperatures due to formation of mixed oxide as support [3]. The $LaAlO_3$ perovskite structure is stable up to 1000 °C. Under reductive atmosphere, the formation of Co^0 was detected at temperatures above 400 °C which is the active species for methane reforming.

All tested catalysts were active in bi-reforming at 700-1000 °C and high water contents (18 vol%) in the feed gas mixture. Using Co-$AlLaO_x$, the conversion of CH_4 was almost complete at 800 °C (see Fig. 1). The high stability of Co-$AlLaO_x$ for CH_4 reforming was confirmed in experiments running more than 40 h.

These results show that by coupling autothermal combustion of biogas and catalytic reforming of the remaining methane at very high temperatures with stable catalysts, synthesis gas yields > 90% are possible, which can be converted, e.g., into methanol in subsequent process steps.

Acknowledgments *The authors would like to thank for the financial support of the project (03EE5070A-D) funded by the Federal Ministry of Economics and Climate Protection.*

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Mechanistic Insights of Total Methane Oxidation over Iron-Containing Beta Zeolites

A. Niederdränk[1,2*], T. Kratky[1,2], J. Schobel[1,2], S. Günther[1,2], O. Hinrichsen[1,2]

[1]*Technical University of Munich, School of Natural Sciences, Garching, Germany*
[2]*Technical University of Munich, Catalysis Research Center, Garching, Germany*
[*]*anne.niederdraenk@tum.de*

Keywords: methane oxidation, iron beta zeolite

Introduction. Due to the growing demand for improved environmental and climate protection, dual fuel and gas-powered marine engines offer high potential in the maritime sector owing to reduced emissions of greenhouse gases (GHG), such as CO_2, NO_x and particulate matter. [1] However, these engines also emit unburnt CH_4, acting as potent GHG demanding for further oxidation of CH_4 to CO_2. Until now, catalysts with platinum group metals have typically been used for total oxidation of CH_4. Due to their high costs, novel non-precious catalysts with high activities and stabilities need to be developed. Iron-containing beta zeolites have already been proven for selective catalytic reduction (SCR) of NO_x in exhaust catalysis. [2] Aiming at a coupling of SCR and methane oxidation, various cheap and non-toxic iron beta zeolites were synthesized and successfully applied in the total oxidation of methane.

Experimental. The investigated catalysts were synthesized by doping commercial beta zeolites with iron nitrate based on wetness impregnation, solid ion exchange, liquid ion exchange and liquid ion exchange modified with sonication. The materials were subsequently calcined at 550 °C. Structural analysis was carried out by means of X-ray powder diffraction, N_2 physisorption analysis, Raman spectroscopy and X-ray photoelectron spectroscopy. Activity measurements were performed under 5000 ppm CH_4 and 19% O_2 in He at temperatures ranging from 220 – 600 °C at pressures up to 3 bar.

Results and discussion. Thorough characterization of the synthesized catalysts has shown that the procedure of iron incorporation into the zeolite affects both, the distribution and the type of iron species incorporated in the zeolite. Preparation by means of solid ion exchange resulted in the formation of a hematite phase. In contrast, no crystalline iron phase could be detected for the other synthesis routes, suggesting a fine dispersion or even an incorporation of iron into the zeolite structure. Activity measurements revealed an impact of iron species on the activity for complete methane oxidation. Here, the catalyst evincing a hematite phase revealed the lowest activity. In order to investigate the active centers for methane oxidation, *in situ* XPS measurements combined with mass spectrometry were carried out on hematite as model system. At ambient conditions, hematite converted CH_4 to CO_2. Temperature-programmed desorption revealed formate as intermediate species. *Ex situ* XPS indicated Fe^{3+} as predominant surface species. Due to the low sticking of CH_4, no carbon could be observed on the surface after the reaction. In order to shed light on the active surface species during catalysis, the oxidation of acetylene over iron oxide was followed by *in situ* XPS making use of the higher sticking of acetylene. Activity measurements at ambient pressure proved a higher activity compared to methane oxidation involving formate species as intermediates. Characterizing the surface *in situ* by XPS also revealed Fe^{3+} as predominant surface species. It could be shown that the novel iron oxide catalysts are very stable against coking and maintain their high activity.

Acknowledgments
The authors acknowledge the financial support by the German Federal Ministry for Economic Affairs and Climate Action.

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Effect of dopants on soot oxidation over doped Ag/ZrO_2 catalysts for catalyzed gasoline particulate filter

L. Nossova[1*], G. Caravaggio

Natural Resources Canada (NRCan), CanmetENERGY–Ottawa, 1 Haanel Drive, ON, K1A 0R6, Canada
[*]lioudmila.nossova@nrcan-rncan.gc.ca

Keywords: soot combustion, catalyzed gasoline particulate filter, doped silver zirconia catalyst

Introduction. Petroleum-based fuels are still the predominant energy used in transportation. Strict energy and environmental policies to fight climate change dictate the necessary improvement of conventional aftertreatment technologies for internal combustion engines. One way to make soot removal from gasoline direct injection (GDI) engine exhaust more efficient is to load a catalyst to a gasoline particulate filter (GPF). This study presents the results for soot oxidation under low oxygen concentration using silver-zirconia catalysts doped with Y, La, Ce and Pr. The gasoline soot oxidation activity of fresh and aged catalysts was compared in view of practical GPF applications.

Experimental/methodology. A series of doped $Ag/M\text{-}ZrO_2$ catalysts (M is Y or La or Ce or Pr) was synthesized by a citric-assisted sol-gel method using metal nitrates as precursors in amounts to obtain 10 wt% of Ag and 8 mol% of M-dopant oxide in the mixed oxide. Before testing, the catalysts were dried at 200°C overnight followed by calcination in air at 550°C for 6 h.

The resulting catalysts were characterized by BET, XRD, XPS and O_2-TPD methods. The fresh and aged catalysts were eveluated for soot oxidation under low oxygen concentration. Carbon black was tightly mixed with a catalyst in a w/w ratio of 1:10.

Results and discussion. During preliminary temperature programmed oxidation (TPO) testing, the $Ag/La\text{-}ZrO_2$ and $Ag/Y\text{-}ZrO_2$ catalysts revealed the best activity and thermal stability among a series of catalysts when tested fresh and after thermal aging at 700°C 6 h. Table 1 shows the testing results of these two catalysts in comparison to the undoped catalyst in the presence of gas components in concentrations simulating stoichiometric GDI exhaust [1]. Similar soot oxidation activity (T_{max} of 405°C) was found for the fresh catalysts modified by La or Y, however, after aging the $Ag/La\text{-}ZrO_2$ catalyst revealed the best stability exhibiting the lowest T_{max} of 419°C of the two. The catalyst modification with La and Y also resulted in improved activity for co-oxidation of CO and C_3H_6, which need to be removed as well. The most reasonable cause for the increase in the oxidative activity and stability of doped catalysts is a combination of changes in textural and structural properties, as well as in the number of oxygen vacancies and the degree of oxygen desorption of modified materials.

Table 1. T_{max} and T_{50} as a measure of catalytic activity for soot oxidation and CO and C_3H_6 co-oxidation of fresh and aged catalysts tested under simulated GDI exhaust conditions. Testing conditions: 12 vol% H_2O, 12 vol% CO_2, 1.5 vol% O_2, 5000 ppm CO, 1000 ppm NO, 500 ppm C_3H_6, balance N_2, tight contact, 250 mg catalyst : carbon = 10:1 w/w ratio, catalyst : cordierite = 1:1 w/w ratio

Catalyst	Soot oxidation T_{max} (°C)		CO oxidation T_{50} (°C)		C_3H_6 oxidation T_{50} (°C)	
	Fresh	Aged	Fresh	Aged	Fresh	Aged
Ag/ZrO_2	425	476	286	395	330	435
$Ag/Y\text{-}ZrO_2$	405	432	257	336	297	379
$Ag/La\text{-}ZrO_2$	404	419	254	308	295	345

Acknowledgments

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Mn substitution of Co in mixed oxides – effect on physical, chemical and catalytic properties in direct NO decomposition

Bílková T.[a], Pacultová K.[a], Fridrichová D.[a], Karásková K.[a], Koštejn M.[b], Jirátová K.[b], Obalová L.[a]

[a] *Institute of Environmental Technology, CEET, VSB-Technical University of Ostrava, Czech Republic*
[b] *Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Czech Republic*

Keywords: nitric oxide, Co-based mixed oxides, K-promoter, structure-activity relationship

Introduction. NO together with NO_2 are known as NO_x, which are mainly produced by anthropogenic activities (combustion of fossil fuels, in cars and industry) and their emissions represent serious environmental problems causing formation of photochemical smog and acid rains. Commonly used methods (selective catalytic reduction and selective non-catalytic reduction) are effective, however, reducing agent (NH_3, urea) is needed. Co-based mixed oxides catalysts modified by K were found to be active in direct NO decomposition [1, 2] producing N_2 and O_2 as the final products. It is known that addition of K to Co oxides ensures the required catalytic properties. Partial substitution of Co by Mg in K/Co_4MnAlO_x was performed [3] and the catalytic activity did not change. It suggests that Co, which is corrosive, toxic and expensive, can be replaced by another metal without loss of activity.

Experimental/methodology. In this study, Mn was used for substitution for Co. The set of samples denoted as $Co_zMn_{5-z}AlO_x$ was prepared by co-precipitation of corresponding nitrates and modified by 2 wt.% of K. Using several characterization techniques (AAS, XPS, XRD, S_{BET} TEM, TPR H_2, TPD CO_2, TPD NO, XAS), the physico-chemical properties of prepared catalysts were studied in relation to their catalytic performance.

Results and discussion. From obtained results, it can be concluded that potassium and Co play the key role in NO decomposition reaction, since the K/Mn_5AlO_x is totally inactive. The increase of NO conversion can be observed up to molar ratio Co/Mn = 3/2, higher amounts of cobalt in the sample do not influence obtained conversion. Presence of manganese affects the catalyst long term stability. The most stable catalyst is K/Co_4MnAlO_x which also showed the largest S_{BET}.

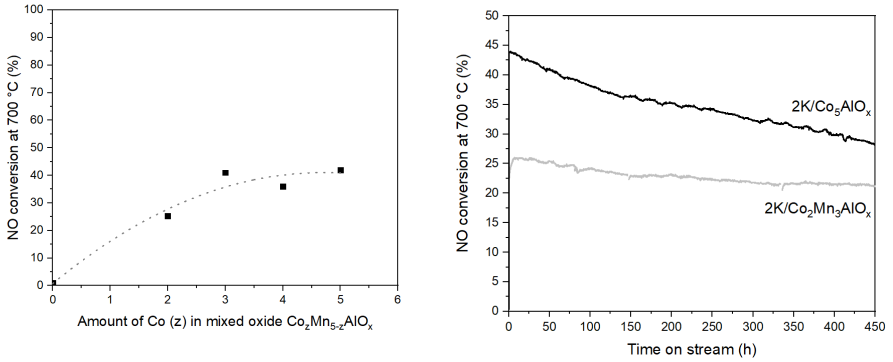

Fig. 1: Dependence of NO conversion (700 °C) on Co molar content in $Co_zMn_{5-z}AlO_x$ mixed oxide (left) and long term stability of selected samples (right). Conditions: 1000 ppm NO in N_2, GHSV = 6 l g^{-1} h^{-1}.

Acknowledgments

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Ni-$LaMnO_3$ nanocomposites as novel PGM-free CH_4 combustion catalysts: effect of synthetic method on catalytic performances

A. Osti[1*], L. Rizzato[1], J. Cavazzani[1], A. Glisenti[1,2]

[1]*Department of Chemical Sciences, University of Padova – via F. Marzolo, 1 – 35131 Padova, Italy*
[2]*ICMATE-CNR, Department of Chemical Sciences – via F. Marzolo, 1 – 35131 Padova, Italy*
[*]*andrea.osti.1@phd.unipd.it*

Keywords: Methane oxidation, Nickel, Exsolution, ADP, Perovskites

Introduction. Methane can represent a renewable and low carbon fuel if derived from biomass anaerobic digestion to biogas, which can be fed in the already existing natural-gas pipelines and vehicles. CH_4 oxidation is a key reaction taking place in post-combustion three-way catalytic converters (TWC) applied to methane-fed vehicles [1]. However, conventional catalytic formulations rely on noble metal particles, especially Pd [2], therefore its replacement with cheaper and more earth-abundant materials would be desirable. Among transition metals, Ni is widely adopted for other CH_4 activation reactions, such as Steam Reforming and Dry Reforming. Perovskites were already found suitable materials to stabilize the dispersion of Platinum Group Metals (PGMs) catalysts, thanks to a self-regenerative process in which PGMs can reversibly exit from and re-enter the perovskite structure in oscillating reducing-oxidizing conditions typical of TWC operating around the stoichiometric air/fuel ratio [3]. There is some evidence that a similar mechanism can also occur for non-noble transition metals like Ni [4]. Based on the above considerations, we hereby propose perovskite-supported Ni catalysts for the complete CH_4 combustion to CO_2. A LaMn-perovskite was chosen, for its good oxidation activity and oxygen storage capacity, with A-site deficient composition ($La_{0.8}MnO_3$), which should favor the generation of oxygen vacancies and thus the absorption of gas-phase reactants.

Experimental/methodology. Perovskites were synthesized by means of the citrate sol-gel route with final calcination in air at 750°C; different citric acid amounts (molar ratio CA/metals = 1.1 or 1.5) were evaluated. Ni was added to the catalytic formulation according to two different methods: i) perovskite B-site doping to obtain $La_{0.8}Mn_{1-x}Ni_xO_3$ (x = 0.1 or 0.2) compositions, followed by Ni^0 exsolution out of the oxide matrix through a reductive treatment in 5% H_2/Ar; ii) Ammonia-driven deposition precipitation (ADP), i.e. Ni^{2+} precipitation onto pre-calcined $La_{0.8}MnO_3$ support by NH_3 addition, followed by calcination in air and reduction to Ni^0 in 5% H_2/Ar. The obtained catalysts were characterized by XRD, XPS, N_2 physisorption, SEM-EDX, H_2-TPR and H_2-pulsed chemisorption. Catalytic CH_4 oxidation tests with stoichiometric O_2 were carried out in a simplified reaction mixture, in the temperature range 300-800°C, with a WHSV of 120 L h^{-1} g^{-1}. Catalytic activity of both freshly calcined and reduced catalysts was evaluated.

Results and discussion. Physicochemical properties of the obtained perovskites were deeply influenced by the amount of citric acid: more favorable surface area, reducibility and availability of surface oxygen species were obtained with molar ratio CA/metals of 1.1 with respect to 1.5, leading to higher CH_4 oxidation activity in the former case. Compared to benchmark $La_{0.8}MnO_3$, B-site Ni doping slightly enhanced catalytic performances at low temperatures, whereas a greater beneficial effect was obtained with NiO-ADP in the whole T range, highlighting the promising activity of Ni^{2+} species. After reduction from NiO to Ni^0, confirmed by XRD, ADP sample did not reveal any significant difference in catalytic performances, whereas a slight improvement was achieved through Ni^0 exsolution from B-site doped compositions. However, the extent of exsolution was rather low since low metal dispersion values were obtained by H_2 chemisorption; an optimization of the exsolution process is therefore required to further improve catalytic performances.

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Facile synthesis of Ir/$LaFeO_3$ catalyst for propene total oxidation

F. Pan[1], W. Zhang[1], C. Ferronato[1], J. Valverde[2], A. Giroir-Fendler[1,*]

[1] *Univ. Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, Villeurbanne, France*

[2] *Department of Chemical Engineering, University of Castilla La Mancha, Ciudad Real, Spain*

[*] *Corresponding Author: Anne GIROIR-FENDLER.; E-mail address: anne.giroir-fendler@ircelyon.univ-lyon1.fr*

Keywords: iridium, perovskite, catalytic oxidation

Introduction. In recent years, volatile organic compounds (VOCs) have become one of the main contributors to air pollution [1]. Catalytic oxidation is one of the most efficient ways to eliminate VOCs. Supported noble metal catalysis is one of the most investigated fields in heterogeneous catalysis because of presenting outstanding catalytic behavior as well as mitigating the rising environmental and energy challenges [2].

Experimental. In this study, Ir/$LaFeO_3$ was synthesized by a facile grinding method [3]. Iridium acetylacetonate and $LaFeO_3$ were ground in a mortar, followed by calcined at different temperatures (300-600 °C). The physicochemical properties of these catalysts were characterized by TG/TDA, ICP analysis, FTIR, XRD, Raman, N_2 adsorption, HRTEM, XPS, and H_2-TPR.

Results and discussion. No characteristic peaks of Ir or IrO_2 were observed in XRD, Raman and FTIR spectra, indicating the high dispersion of Ir on the $LaFeO_3$ support. In addition, no iridium particles or aggregates could be found by HRTEM though EDX analysis demonstrated the presence of Ir element, which probably suggests atomic dispersion of Ir due to the strong interaction with the perovskite. Ir loading hardly changed the specific surface area and orthorhombic structure of $LaFeO_3$, whereas greatly enhanced the reducibility. XPS results indicated the presence of a higher amount of surface Ir^{3+} and adsorbed oxygen species on Ir/$LaFeO_3$-300 than those on Ir/$LaFeO_3$-600. The propene oxidation performance of $LaFeO_3$ was significantly promoted by Ir. All Ir catalysts can achieve 100% propene conversion to CO_2 and H_2O below 320 °C, Ir/$LaFeO_3$-300 being the best catalyst (100% conversion at 250 °C). The catalytic activity decreases with the calcination temperature, which correlates well with the low-temperature reducibility of the catalysts. Moreover, the optimal catalyst Ir/$LaFeO_3$-300 showed decent long-term stability and water resistance.

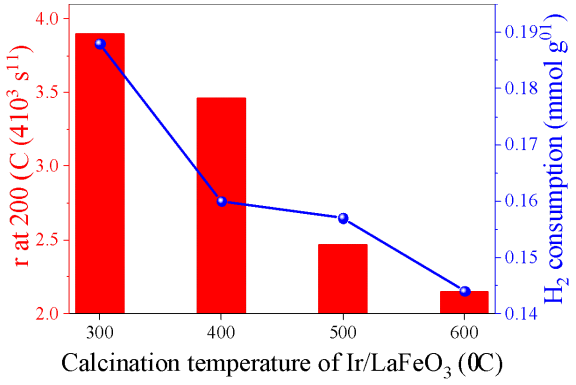

Fig. 1 H_2 consumption in H_2-TPR and propene oxidation rate (r) at 200 °C over Ir/$LaFeO_3$ calcined at different temperatures.

Acknowledgments

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LOW-TEMPERATURE TOLUENE OXIDATION ON Fe-CONTAINING MODIFIED SBA-15 MATERIALS

M. Popova[1]*, I. Trendafilova[1,2], M. Ojeda[3], J.M. Andresen[3], A. Ristic[4], M. Dimitrov[1], N. Novak Tušar[4], G. Atanasova[5],

[1] Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

[2] Laboratory of Inorganic Materials Chemistry, University of Namur, Namur, Namur Institute of Structured Matter, University of Namur, Namur, Belgium (current address)

[3] Research Centre for Carbon Solutions (RCCS), Heriot-Watt University, Edinburgh, United Kingdom

[4] Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Ljubljana, Slovenia

[5] Graduate School, University of Nova Gorica, Nova Gorica, Slovenia,

[6] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

Corresponding Author's E-mail address: margarita.popova@orgchm.bas.bg

Keywords: iron oxides, AlSBA-15, ZrSBA-15, SBA-15, toluene oxidation, VOC removal

Introduction. There are increasing environmental concerns regarding anthropogenic releases of volatile organic compounds (VOCs) that have serious impact on the environment since they are linked to ozone formation, acid rain and formation of fine particles and smog [1,2]. A promising approach for VOCs reduction has been the application of catalytic oxidation. The main challenge to achieving high efficiency of this process is the development of a stable, cost-effective catalytic system with high conversion of VOCs into non-pollutants.

In this study, Fe-containing SBA-15, ZrSBA-15 and AlSBA-15 were synthesized and tested for removal of toluene as a model compound for the oxidation of VOCs. The influence of the synthesis procedure and the chemical composition on the physico-chemical and catalytic properties of the obtained materials was studied.

Experimental. The obtained materials were characterized by X-ray powder diffraction, N_2 physisorption, temperature-programmed reduction (TPR-TGA), TEM and XPS spectroscopy. The reaction of toluene oxidation was monitored at atmospheric pressure using a vertical fixed-bed flow reactor with air as carrier gas (30 ml/min). The air flow was purged through toluene equilibrated at 0 °C ($p_{toluene}$= 0.9 kPa).

Results and discussion. Transition metals as catalysts for total VOC oxidation at low temperatures (150-280 °C) pose a big challenge nowadays. Therefore, iron modified SBA-15, AlSBA-15 and ZrSBA-15 materials with 0.5 to 5.0 wt.% Fe loading were prepared and tested for toluene oxidation. It was found that increasing Fe loading significantly improved the rate of oxidation and lowered the temperature of achieving 100% removal of toluene from above 500 °C for the supports (AlSBA-15 and ZrSBA-15) to below 400 °C for 5FeZrSBA-15. The formation of finely dispersed iron-oxide active sites with a particle size less than <5 nm was observed on all the SBA-15, AlSBA-15 and ZrSBA-15 supports. It was found that the surface properties of the mesoporous support due to the addition of Al or Zr predetermined the type of formed iron oxide species and their localization on the support surface. Fe containing SBA-15 and AlSBEA-15 showed activity in total toluene oxidation at higher temperatures (280 – 450 °C). However, 5 wt. % Fe containing ZrSBA-15 showed excellent activity in total oxidation of toluene as a model VOC at lower temperatures (150 – 380 °C) due to the synergistics effect of Fe-Zr and the presence of accessible and stable Fe^{2+}/Fe^{3+} active sites.

Acknowledgments

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Microwave activation of oxide catalysts for direct oxidation of exhaust gas components

D. Röhrens[1,2,*], A. Abouserie[1,2], X. Wu[1,2], U. Simon[1,2]

[1]*Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1a, 52074 Aachen, Germany*
[2]*Center for Automotive Catalytic Systems Aachen, RWTH Aachen University, 52062 Aachen, Germany*
[*]*daniel.roehrens@ac.rwth-aachen.de*

Keywords: Microwaves, direct oxidation catalysts, mixed-conducting oxides, activation

Introduction.
Recently, microwave-assisted heterogeneous catalysis has gained increased attention as a method to quickly, efficiently and selectively facilitate the catalytic conversion of exhaust gas components[1,2]. In this study we investigated the direct oxidation of carbon monoxide and methane in a microwave-assisted catalysis process employing perovskite (La,Sr)CoO_3 and fluorite type Cu-CeO_2. A microwave-based pre-treatment of the catalyst showed a significant influence on the obtained results.

Experimental/methodology.
A monomode microwave setup was used to heat and activate the granuled catalyst materials in a flow-reactor configuration[3]. The experiments were conducted both in dry and humidified atmosphere to serve as a model environment for the development of a microwave-assisted exhaust aftertreatment process. The concentration of CO in the gas stream was quantified by means of FTIR-spectroscopy. Partially substituted perovskite and fluorite type oxides were synthesized to create materials with both a large number of oxygen vacancies and suitable microwave susceptibility.

Results and discussion.
Our research revealed that the catalysts performance of the materials under investigation depends not only on composition (i.e. the degree of substitution in the oxide lattice) but also on the specifics of a microwave based reductive activation pretreatment. This activation treatment leads to considerably increased catalytic activity with activation energies for dry CO oxidation decreasing from 35.90 kJ/mol (pristine sample) to 23.07 kJ/mol (MW-activated sample) in the case of $La_{0.8}Sr_{0.2}CoO_3$. This approach thus offers the possibility for an efficient low-temperature exhaust aftertreatment process. These results show promising potential for microwave-assisted catalysis in direct oxidation of exhaust gas components and can lead to a better understanding of the material dependant changes of the catalysts under MW-irradiation.

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Analysis of the process of soot removal from diesel engine exhaust with the use of MnO_X-CeO_2 catalysts

M. Rotko[*1], J. Ryczkowski[1], K. Karpińska-Wliżło[1], N. Dubińska[1], P. Moustris[1,2]

[1]*Maria Curie-Sklodowska University, Faculty of Chemistry, Institute of Chemical Sciences, Department of Chemical Technology, Lublin, Poland*
[2]*ERASMUS student from the University of Patras, Patras, Greece*
[*]*Corresponding Author's E-mail address: marek.rotko@mail.umcs.pl*

Keywords: soot oxidation, NO oxidation, MnO_X-CeO_2 catalyst,

Introduction. Soot removal (oxidation) from diesel engine exhaust is a crucial process in terms of environment and health. Soot, due to its size and floating time in the air, is one of the causes of several diseases (e.g. lung cancer) and also contributes to the greenhouse effect. Currently, a common method to prevent the emission of this type of pollutant is the installation of a catalytic diesel particle filter (CDPF) in the engine exhaust system. This solution is based on noble metals, so a cheaper alternative is sought. One such proposal is the use of manganese-cerium mixed oxides, which are active in both direct soot oxidation and NO_X-assisted soot oxidation.

Experimental/methodology. Catalytic materials were prepared by co-precipitation from aqueous solutions of acetate salts by adding ammonium carbonate. The catalyst precursors were dried at room temperature, then at 110°C for 5 hours, and calcined at 500°C for 2 hours. Physicochemical properties were tested using XRF, BET, XRD, Raman, and XPS methods. Catalytic abilities were analyzed in a gas mixture containing oxygen and NO in tight and loose contact.

Results and discussion. The catalysts contain various amounts of manganese and cerium and are characterized by different surface areas, average pore diameter, and the volume of pores (Table 1). The 0.25Mn-0.75Ce catalyst shows the highest activity in the process of soot oxidation both in tight and loose contact (Figure 1). However, in loose contact, the soot oxidation temperature is shifted to a higher temperature by more than 100°C compared to tight contact.

Table 1. Results of XRF and BET analysis.

Catalyst	Metal content (wt. %)		Total BET surface area (m^2/g)	Average pore diameter (nm)	The volume of pores (cm^3/g)
	Mn	Ce			
Mn	71	0	7.5	30.94	0.05
0.75Mn-0.25Ce	40.2	31.7	76.5	7.77	0.14
0.5Mn-0.5Ce	22.6	53.1	101.6	5.81	0.10
0.25Mn-0.75Ce	9.6	70.6	102.0	6.11	0.07
Ce	0	81.2	85.9	5.51	0.04

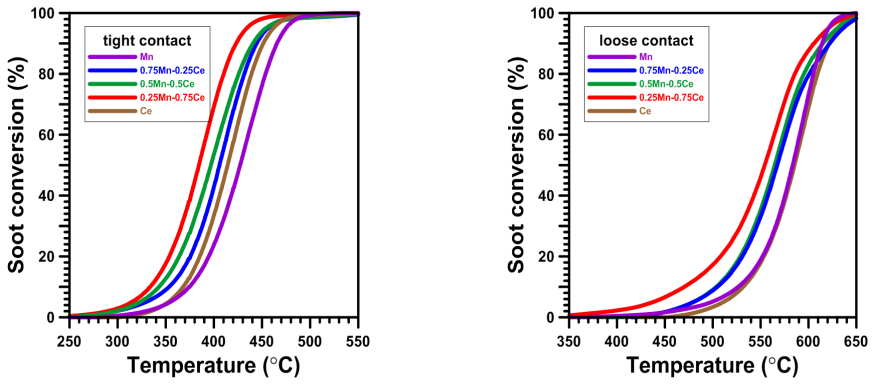

Figure 1. The activity of MnO_X-CeO_2 catalysts in the process of soot oxidation.

One-pot synthesized Fe-ITQ-2 as catalyst for selective catalytic reduction of nitrogen oxides with ammonia – the effect of iron loading

A. Szymaszek-Wawryca[1*], U. Díaz[2], D. Duraczyńska[3], B. Samojeden[1], M. Motak[1]

[1]*Faculty of Energy and Fuels, AGH University of Science and Technology, Al. Adama Mickiewicza 30, 30-059 Krakow, Poland*
[2]*Instituto de Tecnología Química, UPV-CSIC, Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos, s/n, 46022 Valencia, Spain*
[3]*Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Ul. Niezapominajek 8, 30-239 Krakow, Poland*
[*]*Corresponding author: agnszym@agh.edu.pl, bsamo1@agh.edu.pl*

Keywords: layered zeolites, ITQ-2, Fe, one-pot synthesis, $DeNO_x$

Introduction. The zeolites exhibiting MWW morphology found many applications in the industry, mainly because of their well-developed porous texture, mild acid performance, and high hydrothermal stability. One of the interesting representatives of this group is ITQ-2, obtained from the layered precursor, MCM-22 (P) and characterized a delaminated structure, so-called "house of cards" [1]. The unique morphological and chemical features of ITQ-2 make the material an attractive support for the catalyst of the reactions which require micro-mesoporous texture and abundance of acid centers, i.e. selective catalytic reduction of nitrogen oxides with ammonia (NH_3-SCR). One of the major problems related to the industrial catalyst of NH_3-SCR is related to its narrow temperature window and toxicity of the active phase [2]. Hence, the goal of the presented studies was to investigate the catalytic potential of iron-modified ITQ-2 as an alternative, non-toxic catalyst for NH_3-SCR. Since the catalytic performance of metal-zeolites is determined by the speciation of the active phase, we prepared the samples using a one-pot synthesis to promote the incorporation of the isolated Fe^{3+} cations in the framework positions of the zeolite [3]. Additionally, we analyzed the relation between the Si/Fe molar ratio in the samples and their physicochemical and catalytic characteristics.

Experimental/methodology. The series of one-pot synthesized Fe-ITQ-2 samples was prepared according to Chen et al. [3]. The molar composition of the reacting gel was optimized to obtain the samples with Si/Fe molar ratio of 20 or 10. To compare the one-pot synthesis and post-synthesis procedure, the reference catalyst was prepared by the adsorption of Fe^{3+} cations from the aqueous solution. The materials were characterized by ICP-OES, low-temperature N_2 sorption, XRD, UV-Vis, Py-IR sorption, FT-IR, and SEM. The catalytic performance of NH_3-SCR was investigated within 150-450 °C using a model gas mixture consisting of NO, NH_3, O_2, and He as an inert.

Results and discussion. In our work, we have demonstrated that Fe-modified ITQ-2 can be successfully prepared by one-pot synthesis. The introduction of iron into the synthesis gel did not interrupt the formation of MWW layers. The superior low-temperature activity of one-pot synthesized catalysts was related to the abundance of the framework and extra-framework Fe^{3+} cations. Moreover, the decrease of the Si/Fe molar ratio resulted in the formation of bulky aggregates of iron oxide, which contributed to undesired reactions, such as oxidation of ammonia in the high-temperature range.

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Copper effect on the catalytic performance of $LaMnO_3$ for toluene oxidation

C. A. Mendez[1], J.A Gallego[2,3], A. Santamaria[1*]

[1]*Quimica de Recursos Energéticos y Medio Ambiente, Instituto de Química, Universidad de Antioquia, Medellín, Colombia*
[2]*Center for Materials Research, Justus–Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany*
[3]*Institute of Physical Chemistry, Justus–Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany*
[*]*Corresponding Author's E-mail address (Calibri, 11 pt., Italic)*

Keywords: 1, Toluene oxidation 2, Copper effect 3, Perovskites 4, Catalytic activity 5, Volatile organic compounds (VOC).

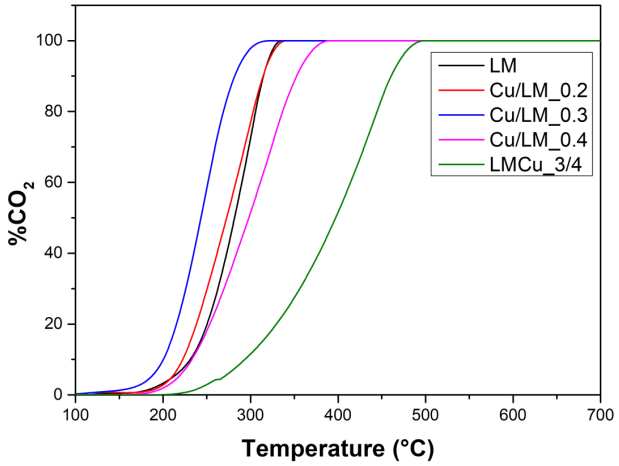

Figure. Copper effect on toluene oxidation

The emission of aromatic VOC impacts not only health but also the environment due to its stability, reactivity, and resistance to oxidation [1]. Catalytic oxidation is presented as a promising alternative to reduce these emissions at low temperature. In this study, the effect of copper addition on the perovskite $LaMnO_3$ (**LM**), towards toluene oxidation efficiency was evaluated [2, 3]. The catalysts were prepared by self-combustion method and the copper addition was carried out by incipient impregnation. The solids obtained were characterized by XRD, XPS, TPD-O_2, TPR-H_2. Catalytic evaluation was carried out using 1000 ppmv of toluene in air and the combustion products (CO_2 and H_2O) were followed by mass spectrometry. The results indicated that the solid (Cu/LM_0.3) increased the efficiency in the oxidation of toluene, reducing the oxidation temperature by almost 50 °C with respect to the perovskite without copper whose T_{50} was 290 °C (See figure). The presence of Cu on the surface favored the reducibility processes in the catalyst and the activation of labile oxygen, since part of the copper migrates into the structure, generating vacancies. However, it was observed that for copper impregnations greater than 0.3, the catalytic activity was detrimental. The same happened when the incorporation of copper was done by doping the structure with similar copper amounts during the combustion synthesis.

Acknowledgments
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Biological air quality: catalytic inactivation of airborne viruses

A. Serrano-Lotina[1]*, A. Vazquez-Calvo[2], P. Llanos[1], A. Gomez-López[1], R. Martin[2], M. García-Castey[2], V. Alcolea-Rodriguez[1], A. Alcamí[2], M.A. Bañares[1]

[1] *Instituto de Catálisis y Petroleoquímica (ICP), CSIC, C/ Marie Curie 2. 28049 Madrid, Spain*
[2] *Centro de Biología Molecular Severo Ochoa (CBMSO), CSIC, C/ Nicolás Cabrera 1. 28049 Madrid, Spain*
*asl@icp.csic.es

Introduction. Airborne transmission is the main propagation vector for respiratory infections such as flu, cold, SARS-CoV-2 and other infections of the lower respiratory tract, which account for 2.5 million deaths every year [1]. The virus aerosols linger in air and remain infectious for hours. In order to avoid infection propagation, technologies of virus inactivation are needed [2]. Here, we propose the use of catalytic filters, for indoor air-cleaning devices; these will inactivate viruses by oxidative stress of their membrane and/or proteins by selectively heating the filter to mild temperatures.

Experimental/methodology. Active oxidative phase was impregnated on two families of filters: ceramic and polymeric. A pre-screening methodology, based on acellular assays, has been developed to evaluate the oxidative potential of the filters thus minimizing biological risk associated with airborne viruses inactivation test. The pre-screening uses organic molecules probe test. A large number of catalytic systems were tested and compared with representative virus inactivation plaque assays in solution, which consist on . These were made with human coronavirus (HCoV-229E), severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) and rhinovirus (HRV-14). Virus inactivation capacity was assessed by quantifying the number of plaque-forming units (pfu) recovered on susceptible cell cultures. The assays were performed by inoculating 100 µL of the virus suspension onto the surface of the polymeric or ceramic filter with and without active oxidation phase(CONTROL). Runs were made at 37 ºC for 1h.

Results and discussion. The acellular oxidative potential (oxidation probe reaction) of different filters was evaluated and compared with its virus inactivation performance in the assays of virus inactivation. A good correlation was observed, concluding that when the oxidation capacity was greater than 60%, the filters efficiently inactivate HCoV-229E virus. The better performing filters were also evaluated for SARS-CoV-2 and HRV-14 inactivation (37 °C, 1 h). Table 1 shows representative viral titer of a catalyic phase on two catalytic materials (C1: ceramic; P1: polymeric) against SARS-CoV-2 and HRV-14. An effective inactivation was observed with both viruses using the two types of filters. This pre-screening approach is used to select those implemented in catalytic filters in an aerosol chamber prepared ad hoc for these analyses in a P2 biological safety lab.

Table 1. Viral titer after treatment at 37 ºC and 1h with ceramic filter (C1) and polymeric filter (P1) (* the detection limit is 5 pfu/mL).

	SARS-CoV-2			**HRV-14**		
	CONTROL	C1	P1	CONTROL	C1	P1
Viral titer (pfu/mL)	$4{\cdot}10^4$	≤ 5*	≤ 5*	$7{\cdot}10^4$	≤ 5*	≤ 25

Acknowledgments
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Pt and Pd-based catalysts for NOx reduction from H_2 combustion engines

Jieling Shao, Phuoc Hoang Ho, Derek Creaser, Louise Olsson*

Chemical Engineering, Competence Centre of Catalysis, Chalmers University of Technology, Gothenburg, Sweden

**louise.olsson@chalmers.se*

Keywords: H_2-SCR, Pd/SSZ-13, N_2 selectivity

Introduction. In view of approaching stringent regulations, especially for greenhouse gas emissions, interest has been raised in carbon-free hydrogen vehicles. To cope with the small but unavoidable amount of NOx produced by internal combustion engines, selective catalytic reduction (SCR) of NOx by H_2 is being investigated as an attractive technology that does not require any additional reductant fluid or gas onboard the vehicles [1]. In this work, we have compared the catalytic performance of PtPd/SSZ13 bimetallic catalysts with their monometallic counterparts and we show that Pd/SSZ-13 catalyst has a superior N_2 selectivity of almost 80% and with a wider working temperature window. But, the NO conversion is lower on Pd/SSZ-13.

Experimental/methodology. SSZ-13 zeolite was synthesized using a hydrothermal method [2]. Pt-, Pd-, and PtPd/SSZ-13 catalysts were prepared by an incipient impregnation technique. The de-greened powder materials were characterized with various techniques such as elemental analysis, CO chemisorption, N_2 physisorption, XPS and STEM. The synthesized catalyst powder was then coated onto a honeycomb monolith (Cordierite, DxL=1.5 cmx2.0 cm, 400 cpsi). Activity tests were performed with a flow reactor with five cycles of heating and cooling over a temperature range of 80 to 500℃ in a typical lean H_2 combustion gaseous mixture consisting of 10% O_2, 5% CO_2, 5% H_2O, 500 ppm NO and 5000ppm H_2 in Ar.

Results and discussion. Figure 1a shows the activity test performance of the 1 wt% Pd/SSZ-13 catalyst regarding the product gas outlet concentrations and NO conversion during H_2-SCR. It is demonstrated that N_2 was the main product and with two maximum formation peaks at around 130℃ and 230℃, respectively. NO_2 was only formed by NO oxidation at temperatures higher than 300°C because hydrogen was mostly consumed by its combustion. The conversion of NO follows the same trend. Figure 1b illustrates that with the same metal loadings, the Pd catalyst has higher maximum N_2 selectivity than the Pt catalyst (80% versus 70%) and also with a wider working temperature window. However, the conversion is lower. The performance of the PtPd bimetallic catalyst is close to the Pt monometallic catalyst, which is not shown here.

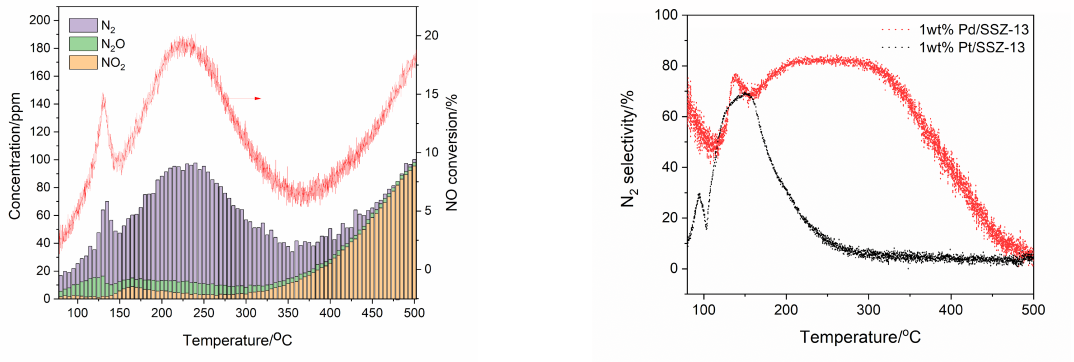

Figure 1. a) Product concentrations and NO conversion of H_2-SCR on 1wt% Pd/SSZ-13 catalyst b) N_2 selectivities of 1wt% Pd/SSZ-13 catalyst and 1wt% Pt/SSZ-13 catalyst (gas inlet: 10% O_2, 5% CO_2, 5% H_2O, 500 ppm NO and 5000ppm H_2).

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Promotional effect of MoO_x for the H_2-deNO_x reaction using Pt/ZrO_2 catalysts

D. Schröder [1], S. Kureti [1,*]

[1] *TU Freiberg, Chair of Reaction Engineering, Germany*
[*] *Corresponding Author: kureti@iec.tu-freiberg.de*

Introduction

For NO_x removal from lean exhaust gases, selective catalytic reduction (SCR) and NO_x storage catalysts are established technologies, whereas they operate efficiently only above 175°C. Contrary, future NO_x emissions limits (e.g. Euro-7) will require an effective abatement of NO_x even at low temperatures. For this purpose, the NO_x reduction by H_2 (H_2-deNO_x) on Pt catalysts is a promising technique. However, these catalysts still suffer from significant N_2O and/or NH_3 by-production. Recently, the modification of Pt/ZrO_2 with W was reported to provide high activity at low temperatures as well as reduced N_2O emissions [1]. The present paper aims the further advancement of the highly active Pt/ZrO_2 catalyst using MoO_x as promising promotor [2].

Methodology

$Pt/xMo/ZrO_2$ catalysts were prepared by incipient wetness impregnation of monoclinic ZrO_2 with aqueous solution of $Pt(NO_3)_2$ and $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$ resulting in a Pt load of 0.25 wt.% and Mo contents between 0 and 10 wt.%. After calcination at 500°C for 5h, the samples were characterized by X-ray diffraction (XRD), N_2 physisorption (BET), temperature-programmed desorption of CO and NH_3, Raman spectroscopy (LRS) and diffuse reflectance infrared spectroscopy (DRIFTS) using NH_3 as probe molecule, while the H_2-deNO_x efficiency was tested in a lean synthetic exhaust (200 ppm NO, 5% O_2, 10% H_2O, 2000 ppm H_2, N_2 balance).

Results and discussion

Fig. 1 clearly shows that promotion of bare Pt/ZrO_2 with Mo leads to a significantly improved low temperature activity, effective suppression of NH_3 emission and increased N_2 selectivity. The Pt/ZrO_2 catalyst with a Mo load of 3 wt.% shows the best performance, including H_2-deNO_x between 80 °C and 150 °C, maximum NO_x conversion of 90% and N_2 selectivity up to 78%. Isolated MoO_x species (LRS) predominately present at Mo loads < 4 wt.% were found to act as structural promoter by stabilizing the surface area, while also providing smaller Pt particles and more active Pt sites (7.1 µmol/g, 3 wt.% Mo) compared to bare $0.25Pt/ZrO_2$ (1.8 µmol/g) as evidenced by CO-TPD. Studies on Pt/ZrO_2 catalysts using in-situ DRIFTS [1] and kinetic modeling [3] showed that the H_2-deNO_x reaction occurs mainly at the Pt sites. Thus, increasing the number of active Pt sites leads to improved activity and N_2 selectivity. However, at Mo loadings > 4 wt.%, the Mo species aggregate and the number of Pt sites decreases, resulting in a drastic drop in H_2-deNO_x activity and N_2 selectivity. Moreover, introducing Mo enhances acidity of Pt/ZrO_2 with formation of new Brønsted and strong Lewis acid sites (NH_3-TPD, DRIFTS). In particular, strong Lewis acid sites were found to improve both, activity in SCR experiments (100 ppm NO + 100 ppm NH_3) and N_2 selectivity in H_2-deNO_x tests. These results suggest that the Mo promotion of Pt/ZrO_2 enables an additional SCR-related mechanistic deNO_x pathway involving strong Lewis acid sites at the MoO_x entities [4]. It is assumed that NH_3 or NH_x species formed on the Pt sites during H_2-deNO_x spill over to the strong Lewis acid sites at highly dispersed MoO_x moieties, followed by a reaction with NO at the interface between the Pt sites and MoO_x. Thus, our study highlights the particular importance of acidity to improve the activity and selectivity of lean H_2-deNO_x catalysts.

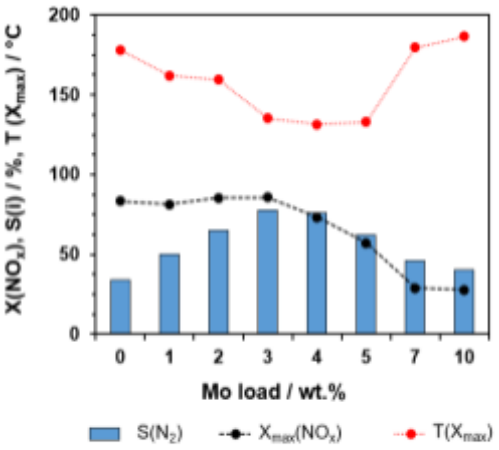

Fig. 1: Maximum $X(NO_x)$, corresponding $T(X_{max})$ and $S(N_2)$ of $0.25Pt/xMo/ZrO_2$.

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Effect of Fe and Ce in a manganese titania catalyst for the low-temperature catalytic reduction of NOx with NH_3

Cristina I. Q. Silva[1*], Polina Lavrik[1], Mohamed Nejib Hedhili[2], Sudheesh Kumar Veeranmaril[1], Sarah Komaty[1], Javier Ruiz-Martínez[1]

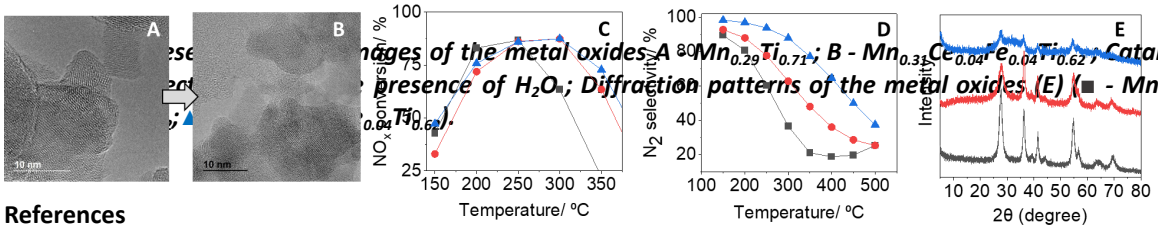
[1]*King Abdullah University of Science and Technology, KAUST Catalysis Center, Thuwal 23955, Saudi Arabia*
[2]*King Abdullah University of Science and Technology, KAUST Core Labs, Thuwal 23955, Saudi Arabia*
[*]*cristina.queirosdasilva@kaust.edu.sa*

Keywords: Low-temperature NH_3-SCR of NO_x, Mn-based metal oxides, heterogeneous catalysis.

Introduction. Nitrogen oxides (NO_x) are harmful pollutants present in combustion gases that can be emitted from stationary and mobile sources. Mn-based oxides are promising for the selective catalytic reduction (SCR) of NO_x with NH_3 at temperatures below 200 °C, where the current commercial deNO_x catalysts fall short.[1, 2] However, MnOx often suffer from low N_2 selectivity and low tolerance for H_2O and SO_2, which can be improved by combining Mn with other transition metals.[1]

Experimental/methodology. We have developed a series of catalysts based on Mn, Fe, Ce and Ti with different compositions by a co-precipitation method designed to obtain a homogeneous dispersion to understand the effect of Fe and Ce in a MnTiOx catalyst. The catalytic activity and N_2 selectivity were tested for NH_3-SCR of NO_x and the properties of these catalysts were investigated by ICP, N_2-physisorption, XRD, H_2-TPR, NH_3-TPD, STEM/EDX, TEM/EELS, XPS and XAS.

Results and discussion. We were able to determine that the addition of Fe to MnTiOx led to a catalyst composed of a rutile TiO_2 structure with well-dispersed amorphous Mn and Fe (Fig.1 (A, E)). The addition of Fe had a detrimental effect on the specific surface area compared to the initial MnTiOx, which had a negative effect on the catalytic activity at low temperatures (below 250 °C) of most samples, particularly in the presence of H_2O (Fig.1 (C)). On the other hand, there was an overall increase in the N_2 selectivity (lower N_2O production) across the tested temperature range (Fig.1 (D)). Based on our previous results [2], we included Ce in the catalyst formulation to improve specific surface areas and consequently catalytic activities. Adding Ce to MnFeTiOx led to a progressively more amorphous structure (Fig.1 (B, E)), higher overall surface areas, higher acidity and better N_2 selectivities in the presence and absence of H_2O. We found an optimum formulation by adding small quantities of Ce and Fe to the MnTiOx catalyst, more specifically in the $Mn_{0.31}Ce_{0.04}Fe_{0.04}Ti_{0.62}$ sample where the catalytic performance and N_2 selectivity were maximized at 150 °C (79% and 94% in the absence of H_2O and 47% and 98% in the presence of H_2O, respectively), while also having a broader temperature range of application (Fig.1 (C, D)). We suggest that the addition of Fe and Ce suppresses overoxidation of reactants and thus N_2O formation by reducing the MnOx ensembles on the catalyst surface.



ges of the metal oxides. A - $Mn_{0.29}Ti_{0.71}$; B - $Mn_{0.31}Ce_{0.04}Fe_{0.04}Ti_{0.62}$; Catalytic activity presence of H_2O; Diffraction patterns of the metal oxides (E) (■ - $Mn_{0.29}Ti_{0.71}$; ● - $_{0.04}Ti_{0.62}$).

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Cobalt-Manganese and Iron-Manganese Mixed Oxide Catalysts for the Total Oxidation of Dimethyl Ether in Flue Gases from Formaldehyde Production Plants

M. Smyrnioti, V. Dracopoulos, T. Ioannides*

Foundation for Research and Technology-Hellas, Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Patras, Greece
**E-mail: theo@iceht.forth.gr*

Introduction. Flue gases from the industrial production of formaldehyde contain CO, methanol, dimethyl ether, H_2O vapor, O_2, N_2 and traces of formaldehyde. The emission control technology applied in the process is based on the catalytic oxidation (incineration) of the flue gases. Even though the concentration of dimethyl ether in the flue gases is low, dimethyl ether dictates the final temperature required for the complete removal of the pollutants since it is the most difficult to oxidize compound compared to CO or methanol. The state-of-the-art catalysts are based on noble metal (Pt, Pd)/γ-Al_2O_3 washcoated on monolithic substrates. The current catalytic converter has a long lifetime, yet it has some shortcomings including its high cost due to the presence of noble metals as well as significant input energy requirements for preheating the feed stream (T_{inlet}>250°C). The present work refers to the development of a new emission control system (ECS) for formaldehyde production plants, based on non-noble metal catalysts; mixed cobalt-manganese oxide ($Co_xMn_{3-x}O_4$, 0<x<3) and iron-manganese oxide ($Fe_xMn_{3-x}O_4$, 0<x<3) catalysts.

Experimental/methodology. The catalysts have been prepared via the citrate complexation method. N_2-physisorption, p-XRD, SEM, XPS, H_2-TPR and CO/VOC-TPD were employed for the physicochemical characterization of the samples. The catalysts have been prepared both in powder and monolithic form while their catalytic activity and long-term stability have been evaluated in the total oxidation of dimethyl ether as well as under a realistic flue gas mixture both on a lab- and a semi-pilot scale.

Results and discussion. The prepared Co-Mn and Fe-Mn mixed oxide catalysts were found to be among the most active catalysts for the total oxidation of dimethyl ether reported so far, with complete DME conversion being achieved at 210 °C (Co-Mn) and 240 °C (Fe-Mn) at GHSV=36000 h^{-1}. The citrate complexation method leads to either the formation of a solid solution (for Fe-Mn catalysts) or spinel phases (for Co-Mn catalysts) with a surface enrichment in manganese being observed throughout the whole composition range in both catalytic systems. The presence of water vapor in the feed stream inhibits the oxidation reaction, shifting the required temperature for the complete DME conversion to CO_2 towards higher temperatures by 20-30°C. Comparing the oxidation of the flue gas mixture with the single gases, it is concluded that the presence of VOCs inhibits the oxidation of CO and vice versa, leading to a shift of the activity curves towards higher temperatures by ~20-25 °C in both cases. The Co-Mn mixed oxide catalysts succeed in narrowing down the significant temperature gap between the oxidation of CO & CH_3OH, on one hand, and DME on the other compared to the prior art (the gap is 70 °C for Co-Mn vs. >160 °C for noble metal-based catalysts [1]). The optimal catalysts were scaled-up on a semi-pilot scale (50x times compared to the lab-scale catalytic tests) in order to study their long-term stability. The mixed oxide catalysts demonstrate exceptional stability retaining their initial activity with no evidence of deactivation for >500 h on-stream during non-isothermal operation of the monolithic reactor. The light-off temperature for the complete conversion of the flue gases (X_{CO} and X_{CH3OH}=100%, X_{DME}=98.5-99%) is 147 °C i.e. ~100°C lower than the current situation, while the reactor outlet temperature is 235 °C due to the exothermicity of oxidation reactions.

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High-throughput synthesis of new up-scalable SCR catalysts and reaction characterization

Sebastian Amann [1], Thomas Schwarz [1], Klaus Stöwe [1], Fei Wen [2]

[1] *Chemnitz University of Technology, 09111 Chemnitz, Germany*
[2] *Umicore AG & Co. KG Hanau, 63457 Hanau, Germany*
[*] *sebastian.amann@chemie.tu-chemnitz.de*

Keywords: High-Throughput; NH_3-SCR; catalysis; mixed oxides

With the guidelines of the emission standards in the EU it is still of high concern to minimize the NO_x emissions of combustion engines of automobiles which are harmful to the environment. The most common catalysts for the removal of NO_x from Diesel engine exhaust gases are either zeolite-based catalysts exchanged with Cu or mixed oxide catalysts of the type $V_2O_5/WO_3@TiO_2$. They are either expensive to produce or show only a limited operational window with a high NO_x conversion rate. [1,2]
Different mixed oxide catalysts based on the carrier material CeO_2 were synthesized via a High-Throughput (HT) approach by a co-impregnation method. Subsequently the conversion rates were measured through HT screening on a motorized linear x-y-z translational shift unit with a catalyst library on a steel sample plate [3,4,5] and gas inlet and outlet by capillaries with a total gas flow of 60 mL/min and a GHSV of 130000 h^{-1} connected to a heated gas cell of a FTIR spectrometer. To validate the conversion rates of the different catalyst systems on the HT x-y-z unit, they were also tested in a conventional gas flow tubular reactor.
Synthesizing a composition spread of selected hits, the conversion rates were further optimized. Both results are shown together with the experimental setup for HT screening in Figure 2.

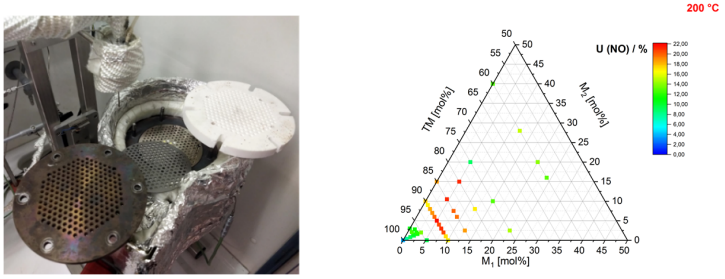

Figure 2: Photograph of the experimental setup for the HT screening of the catalyst library on the x-y-z translational shift unit [left side] and ternary phase diagram for the optimization of selected catalyst samples [right side].

To test the tolerance of the different catalyst systems the NO_x conversion rates were compared before and after an aging procedure with either H_2O or SO_2. The catalysts showed a good tolerance against H_2O depending on the promotional elements used. SO_2 tolerance measurements showed a partial regeneration of the NO_x conversion after a high temperature annealing at 500 °C. Furthermore, the catalysts were characterized regarding their morphology (BET/PXRD/ESEM) and in terms of reaction parameters (NH_3-TPD/H_2-TPR/DRIFTS). The characterization of the catalysts showed a high dispersion of the promotional elements on the carrier material, which also influences the surface properties, an increasing NH_3 adsorption rate for selected elements, different redox properties depending on the catalyst composition and the reaction mechanism showed two possible reaction routes via a Langmuir Hinshelwood or an Eley Rideal mechanism, with the latter being predominant. Through the entire process it was possible to select a catalyst system from the sample library, which could be scaled up and will be further investigated as an alternative mixed oxide catalyst for the NH_3-SCR in Diesel combustion engines of automobiles.

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Composites of Zeolite Y and Cu-Containing Mixed Metal Oxides as Catalysts for NH_3-SCR-DeNO$_x$

Rujito S. R. Suharbiansah[1], Muhammad Fernadi Lukman[2], Alejandro Molla Robles[1], Andreas Pöppl[2], Roger Gläser[1] , Magdalena Jabłońska[1*]

[1]*Institute of Chemical Technology, Universität Leipzig, Linnéstr. 3, 04103 Leipzig, Germany*
[2] *Felix Bloch Institute for Solid State Physics, Universität Leipzig, Linnéstr. 5, 04103, Leipzig, Germany*
[*]*magdalena.jablonska@uni-leipzig.de*

Keywords: Copper, Zeolite Y, Mixed Metal Oxides, NH_3-SCR-DeNO$_x$

Introduction. The selective catalytic reduction of NO$_x$ by ammonia (NH_3-SCR-DeNO$_x$) is the most efficient technology to eliminate NO$_x$ from stationary and mobile sources. Recently, hybrid catalysts combining components of intended functionality have attracted interest for the NH_3-SCR-DeNO$_x$ [1]. For example, the combination of the acidic sorption sites for NH_3 leading to the formation of a reservoir of ammonia molecules can be coupled with highly active metal sites for reaching sufficient activity at low temperatures. Thus, we report the preparation and experimental study of hybrid catalysts consisting of zeolite Y and Cu-containing hydrotalcite-derived CuMgAl-O$_x$ mixed metal oxides.

Experimental/methodology. Zeolite Y (ZY) used in this work was prepared by a dense gel method using a molar composition of $8Na_2O : 1Al_2O_3 : 10SiO_2 : 410H_2O$ [2]. The CuMgAl hydrotalcite-like precursor was prepared by using a coprecipitation method with metal nitrates [3]. For the preparation of the composites, two methods were applied, i.e., a physical and a chemical mixture (abbreviated PM and CM, respectively). All Cu-containing materials were investigated in NH_3-SCR-DeNO$_x$, and thoroughly physico-chemically characterized with respect to their structure and morphology (XRD, SEM), texture (N_2 sorption), and redox/acid properties (H_2-TPR, EPR, DR UV-Vis).

Results and discussion. The SEM images in Fig. 1a show the successful preparation of the zeolite Y / Cu-containing mixed metal oxide composites. There is no significant difference between the materials obtained *via* PM and CM methods, whereas the structure of zeolite Y is still maintained. The morphology represents a well-developed layered and plate-like structure of the CuMgAl mixed metal oxides. Pure zeolite Y reaches less than 4 % NO conversion in NH_3-SCR-DeNO$_x$ (Fig. 1b). The catalytic activity does not vary significantly for the samples prepared *via* PM or CM. The CuMgAl mixed metal oxides and their physical mixture with zeolite Y reveal similar catalytic activity above 300 °C due to the unselective oxidation of NH_3. Thus, the hybrid samples can be considered a promising catalyst for the selective catalytic oxidation of ammonia into nitrogen and water vapor (NH_3-SCO). The studies will be further extended for the preparation of MgAl mixed metal oxides mixed with Cu-containing zeolites.

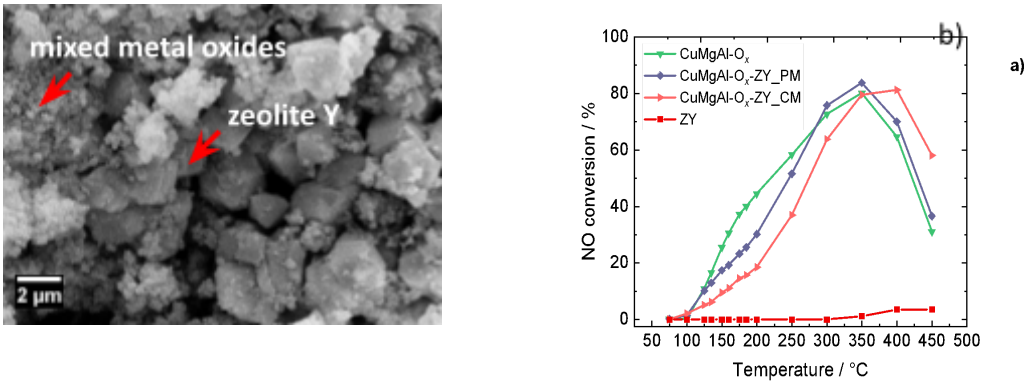

Figure 1. SEM images of CuMgAl-O$_x$/ZY_CM (a) and NO conversion in NH_3-SCR-DeNO$_x$ over CuMgAl-O$_x$/ZY (b).

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Intensified POCS supports with optimized strut geometry for catalytic reactors

Claudio Ferroni[1], Mauro Bracconi[1], Matteo Ambrosetti[1], Matteo Maestri[1], Gianpiero Groppi[1] and Enrico Tronconi[1*]

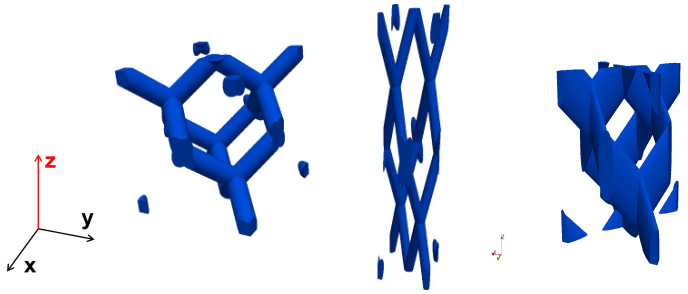
[1]*Laboratory of Catalysis and Catalytic Processes, Department of Energy, Politecnico di Milano, Via La Masa 34, 20156 Milano, Italy*
**enrico.tronconi@polimi.it*

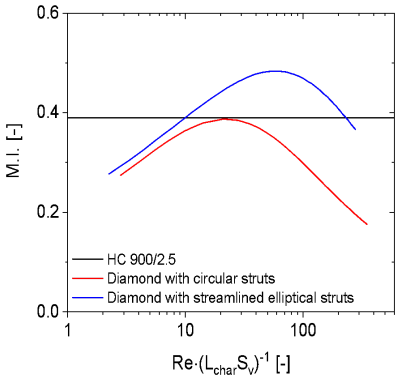
Keywords: Catalytic Reactors, Process Intensification, Structured Catalysts, Lattice Supports

Introduction. 3D printed Periodic Open Cellular Structures (POCS) with Diamond unit cell [1-3] are regarded as promising structured supports to intensify catalytic reactors where the trade-off between gas-solid mass transfer and pressure drop is crucial, like in many important Environmental Catalysis applications. These systems usually employ honeycomb monoliths as reference catalyst supports [3]. Previous investigations revealed that the increment of mass transfer granted by POCS comes along with significantly higher pressure drop. To overcome this drawback, we propose a new geometry that adopts streamlined elliptical struts along the flow direction to reduce the pressure drop.

Experimental/methodology. Reactive CFD simulations are exploited as synthetic experiments for the investigation of transport properties and pressure drop of POCS [3]. Periodic boundary conditions at the domain side boundaries are applied to evaluate asymptotic transport properties as a function of geometrical and operating conditions, neglecting entrance effects and solid wall constraints. The performances are assessed by considering the Merit Index (M.I.), a dimensionless trade-off index relating the mass transfer coefficient with the pressure drop [3].

Results and discussion. Based on the Diamond unit cell ((Figure 1 *(a)*)), the new geometry (Figure 1 *(b)*) is obtained by replacing the cylindrical struts with streamlined elliptical struts along the flow direction (z). Figure 1 *(c)* compares POCS with a honeycomb monolith (HC) 900 CPSI/2.5 mils. The standard Diamond offers poorer performance than the HC due to the greater pressure drop [3]. Conversely, the optimized structure provides up to 25% higher M.I. granted by the reduced pressure losses. Consequently, these structures grant higher conversions than honeycombs for the same pressure drop on a wide range of flowrates. This increment may pave the way towards intensified catalytic reactor solutions.





(a) *(b)* *(c)*

Figure 1 *(a)* Conventional Diamond lattice and *(b)* Diamond using streamlined elliptical struts along the flow direction *z* of the reference system. *(c)* Merit Index of structured supports.

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Improving Sulphur Resistance in Low Temperature Specific SCR Catalysts

A. Sagar[1], M. Casanova[1], M. Czakler[1] H. Solt[2], G P Szijjártó[2], G. Novodárszki[2], A. Tompos[2], B. Truscott[1]

[1]Treibacher Industrie AG, Auer-von-Welsbach-Straße 1, 9330 Althofen, Austria
[2]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Magyar tudósok krt. 2, H-1117 Budapest, Hungary

***byron.truscott@treibacher.com**

Keywords: Selective Catalytic Reduction, SCR, NOx, deNOx, SO_2, Sulphur, ammonium bisulphate, ABS

Abstract-
Selective Catalytic Reduction (SCR) is an important tool for reducing NOx in flue gases. In particular, the use of vanadium oxides on titania is widely utilized and successful owing to relatively good resistance to sulphur poisoning. Industrial flue gases *eg.* those from cement factories, waste incinerators *etc.* inherintly have trace amounts of SO_2 of varying concentrations. SO_2 is oxidised to SO_3 and subsequently reacts with NH_3 to form ammonium bisulphate (ABS). ABS condenses as a liquid in the pores of said catalyst, inhibiting the ability of active sites to function as normal. This results in activity loss and ultimately, deactivation of the SCR catalyst. The ability to perform SCR at low temperatures is importortant for industrial flue gases to mitigate heating costs but ABS fouling poses a significant barrier to deoployment. In this study we will reveal how we have employed intelligent catalyst design and assesment using high throughput screening and performance modelling including Artificial Neural Networks (ANN) and Partial Least Squares (PLS) regression to predict catalyst activity and fouling resistance and how our findings might guide the development of novel SCR catalysts.

Role of Ionic Liquids as Promoters to Enhance CO_2 Capture Performance of Methyldiethanolamine

S. C. Tiwari*, K. K. Pant and S. Upadhyayula

Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India

Corresponding Author's E-mai:l suryact.che16@itbhu.ac.in

Keywords: CO_2 Capture, Dual Funtionalized Ionic Liquid, Kinetics Study

Introduction. CO_2 containing industrial flue gas effluent streams are a potential cause of air pollution. CO_2 capture utilising benign, low-cost solvents is an important unit operation not just in the process sector for CO_2 separation and recovery from industrial off-gas streams, but also for direct capture from air to clean the environment. Researchers have found many solvents with excellent CO_2 capture efficiency owing to their attractive chemical and physical characteristics, CO_2 interaction mechanism, and low regeneration energy cost. However, alkanolamines, such as Monoethanolamine (MEA), Diethanolamine (DEA), and Methyldiethanolamine (MDEA), are the most often utilised solvents for CO2 capture. These solvents have a number of drawbacks, including limited thermal stability, the generation of heat-stable salts, and the fact that they are highly degradable. To address these difficulties, a new type of solvent need be developed. These constraints may be circumvented by dual functionalized ionic liquids (DFILs). Hence, this work a new class of dual functionalized ionic liquids (DFILs) synthesized by the acid-base neutralization reaction using polyamine as cation and cyclic amines as anions.

Experimental/methodology. In this work, the CO_2 absorption was performed using a VLE setup, and the mass balance method was used to calculate the CO_2 loading at different temperatures, pressures, and DFILs concentrations. Further ^{13}C NMR was used to understand the CO_2 interaction with CO_2, which was also validated with DFT results. Additionally, non-linear regression and machine learning methods were used and described to predict the CO_2 loading using 54 data points of CO_2 loading in the DFILs blend MDEA system. Furthermore, specific energy consumption and productivity for all absorbents were calculated, and a comparative study was conducted to select the best promoter.

Results and discussion. Initially, crucial properties such as viscosity and density were measured for these absorbents, and results showed that with increasing wt% of DFILs, viscosity and density slightly increased. CO_2 absorption was also performed, and it was discovered that the CO_2 loading and rate of absorption increased significantly with increasing wt% of DFILs. For the prediction of CO_2 solubility in MDEA blend systems, machine learning methods have been used and predicted. Here, five different methods are applied for prediction, with the MLR, RF, and DTR methods showing high accuracy while the KNN and SVM methods predict with slightly lower accuracy. Further, specific exergy consumption and productivity were calculated for all absorbents, and based on these values, a superior promoter was selected, and it was noticed that [T-Im] and [D-Pz] blend absorbents provided optimum conditions for efficient CO_2 absorption.

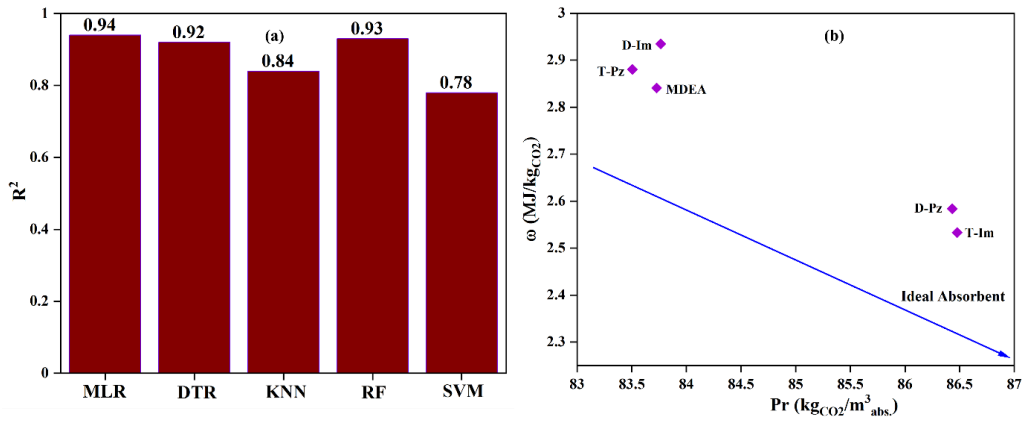

Figure 1. Comparative study for capturing performance: (a) Machine learning methods for CO2 solubility prediction; (b) Economic point of view comparative study of MDEA and MDEA blend MDEA system

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Cu-doped CeO_2 needle-shaped nanocatalysts for low temperature CO oxidation

Xiaochao Wu [1, 2 *], Maria Meledina [3], Cigdem Ozsoy-Keskinbora [3], Ulrich Simon [1, 2]

[1] *Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1a, 52074 Aachen, Germany*
[2] *Center for Automotive Catalytic Systems Aachen, RWTH Aachen University, Aachen, Germany*
[3] *Thermo Fisher Scientific, Materials & Structural Analysis, Achtseweg Noord 5, 5651 GG Eindhoven, the Netherlands*
* *Corresponding Author's E-mail address: xiaochao.wu@ac.rwth-aachen.de*

Keywords: Cu-doped ceria, nanoneedle, oxygen vacancy, CO oxidation reaction

The presence of oxygen vacancies in the CeO_2 crystal lattice, which are participating in the gas adsorption, plays a critical role in the catalytic performance [1, 2]. Thus, an optimized crystal design would help to expose more surface oxygen vacancies, resulting in the enhancement of catalytic activity. Herein, a series of Cu-doped CeO_2 needle-shaped nanocatalysts were synthesized. The oxygen vacancy content was studied and the influence of Cu amount on the CO conversion activity was also investigated. The relationship between the crystal structure and the catalytic activity are discussed.

The as-prepared CeO_2 particles are needle-like shaped with high crystallinity, and the inserted schematic diagram illustrates the assumed nanoneedle grow along the [110] direction (Fig. 1a). When Cu was doped into CeO_2, the distribution of Cu tends to form clusters (Fig. 1b). The detailed mapping image was taken from the surface of CeO_2 (Fig. 1c). The Ce^{3+} are mostly distributed on the surface, while the Ce^{4+} are in the bulk, indicating the present of amounts of oxygen vacancies. By calculating the ratio of Ce^{3+}/Ce^{4+} from the Ce 3d XPS spectrum (Fig. 1d), it can be obtained that the incorporation of 10% Cu formed the most oxygen vacancies on the surface. The CO conversion temperature is in line with the trend of oxygen vacancies concentration (Fig. 1e), suggesting that the vacancies act as active sites for CO adsorption. The DRIFTS result indicates that the 10% Cu doped CeO_2 exhibits rapid CO absorption at room temperature (Fig. 1f).

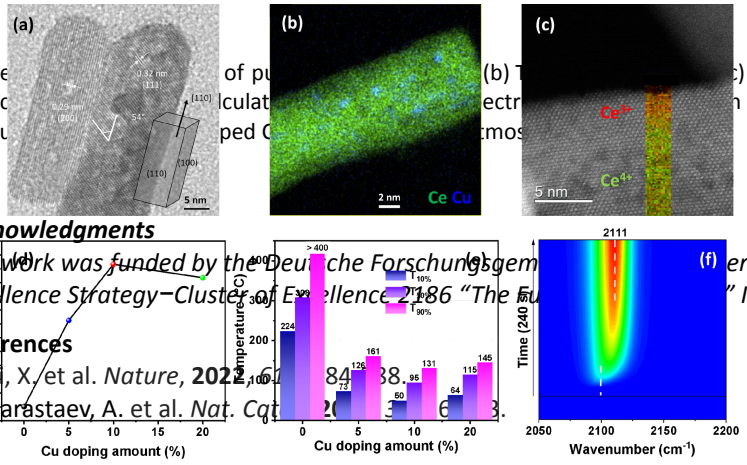

Figure 1 of pu (b) T C) HAADF-TEM image of 10% Cu doped CeO_2, (d) the surfac lculat ectr n performance of Cu doped CeO_2 nanocatalysts, (f) in-situ ped C tmos

Acknowledgments

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Maximizing the CuO/Co_3O_4 interface for N_2O emission control

Zhangyi Yao,[1] Xuze Guan, [1] Lu Chen, [2] and Ryan Wang,*
[1, 2] *University College London, Roberts Building, London, UK*
[*] *ryan.wang@ucl.ac.uk*

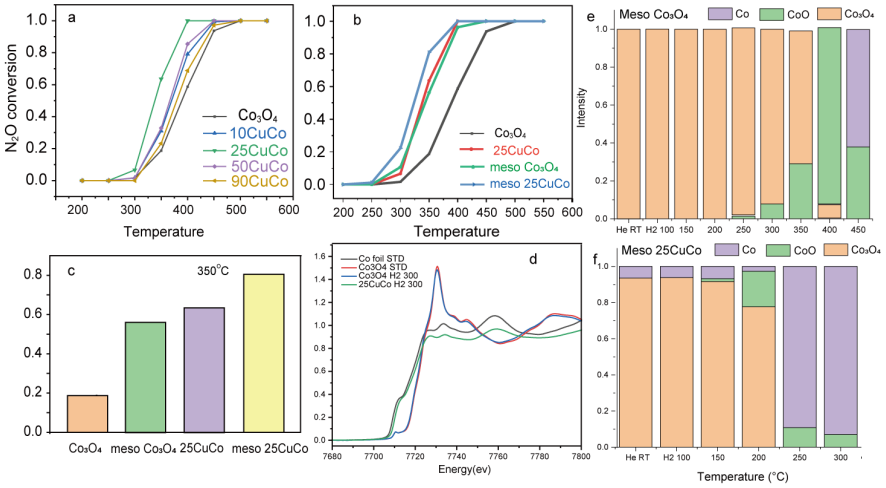
Keywords: EXAFS; N_2O decomposition; Cobalt Oxide; Mesoporous materials; catalysis

Introduction.

Compared to CO_2, the most common green house gases, N_2O has 300 times effect for global warming for a 100-year timescale.[1] Although agriculture is considered as the major source of N_2O due to human activities, the N_2O emission from transportation sector cannot be ignored with 56mg of N_2O/km for on-road vehicles travelling.[2] One of the best N_2O removal ways is catalytic N_2O decomposition. The catalytic process involves breaking N-O bond and forming O* with O_2 as final product, which is a redox reaction. Although nobal metal shows good activity in low temperature, the development of non-noble metal catalytic with excellent redox properties and thermal stability is more important. Our studies use copper and cobalt as materials to design the experiment of how to improve the N_2O conversion.

Experimental/methodology.

We developed a bifunctional catalyst contains both Cu and Co. 1) **Optimizing the loading of Cu.** We have designed five catalysts: Co_3O_4, 10CuCo, 25CuCo, 50CuCo and 90CuCo. The number indicate the concentration of copper loading on Cobalt. With the adding of small amount of Cu, the N_2O conversion was improved significantly especially at low temperature. Most of them show better decomposition ability than pure Co_3O_4 (Fig. 1a). 25 wt% CuO-Co_3O_4 gives 3.5 times higher N_2O conversion than Co_3O_4 at 350 °C, and N_2O can be completely converted at 400 °C. 2) **Maximizing the reactive surface.** We have further improved the activity by synthesizing mesoporous meso-Co_3O_4 and meso-25CuCo that maximize the reactive surface. Meso-25CuCo is by far the best catalyst for N_2O decomposition, surpassing all the reports in the literatures, achieving almost 80% conversion already at 350 °C (Fig. 1b,c).



3) **Reduction of Cu and Co species.** In addition, we performed *in-situ* H_2-TPR XAFS study at spring-8 for meso-Co_3O_4 and meso-25CuCo. For pure Co_3O_4, the reduction starts at 250 °C and to pure Co_3O_4 at 400 °C (Fig. 1e). For meso-25CuCo, the reduction starts at 200 °C and forms majority of metal Co at 250 °C (Fig. 1f). The addition of Cu significantly promotes the reduction of Co^{3+} to Co^0, which is a complete surprise to us.

Figure 1 a,b The conversion of N_2O from 200°C to 550°C. **c,** The comparison of N_2O conversion between non-porous and mesoporous catalysts at 350 °C. **d,** *in-situ* XANES spectra at 300°C under H_2. The LCF(Linear combination fitting) of **e,** meso-Co_3O_4; **f,** meso-25CuCo under H_2 at different temperatures.

Results and discussion.

For N_2O decomposition process, we achieve high surface area *via* templated synthesis; and we also maximize the CuO/Co_3O_4 interfaces by varying the Cu and Co ratio. The templated CuO-Co_3O_4 has a surface area of 91 m^2/g and shows 2.5 times N_2O conversion to that of normal CuO-Co_3O_4 *via* co-precipitation methods. The 25% CuO loading achieves the best N_2O conversion at low temperature. Then we did in-situ XAS study in H_2 atmosphere to confirm that Cu promotes and accelerates the Co^{3+} reduction. Such study is very rare to the N_2O chemistry and will help understand the N_2O decomposition mechanism.

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Catalytic oxidation of propane over Pt-Pd bimetallic nanoparticles supported on TiO_2

R. Camposeco, A. E. Torres, V. Maturano, R. Zanella*
Instituto de Ciencias Aplicadas y Tecnología, Universidad Nacional Autónoma de México, C. U., 04510, Ciudad de México, Mexico
**rodolfo.zanella@icat.unam.mx*

Introduction. The internal combustion engines in vehicles and stationary sources using diesel and gasoline cause harmful pollutants such as carbon monoxide (CO), un-burned hydrocarbons (HCs), nitrogen oxides (NO_x), sulfur oxides (SO_x), and particulate matter (PM). In contrast, liquefied petroleum gas (LPG) is a cleaner alternative to burning fuel in internal combustion engines. Propane is the most abundant light alkane among the organic compounds emitted from combustion of LPG. Noble metals have been found to be highly effective but expensive in the total oxidation of VOCs. Platinum and palladium are some of the most active materials for hydrocarbon oxidation, however, there is debate in the literature about how platinum particle size or shape affects the catalyst activity. In this context, some studies have shown that the reaction rate per platinum atom does not significantly change with the particle size or dispersion, the reaction rate per surface platinum atom increases with larger platinum particle sizes. Up to now, several catalysts have been applied for total propane oxidation and noble metal catalysts have been reported to show better catalytic performance than transition-metal-oxide catalysts.

Experimental/methodology. The mono and bimetallic platinum and palladium catalysts were prepared by the sol-gel method. They were characterized by XRD, ICP-OES, N_2 adsorption/desorption isotherms using the BET method, Pyridine thermo-desorption, H_2-TPR, HRTEM and HAADF, XPS and CO-DRIFTS. The catalytic activity for both reactions was evaluated by temperature programmed experiments using a flow reactor at atmospheric pressure. The reactor output gases were analyzed with an on-line gas chromatograph equipped with TCD and FID detectors and a methanizer to detect CO_2 and/or CO.

Results and discussion. The results show that the catalytic properties of the bimetallic Pt-Pd/TiO_2 catalyst in the propane oxidation reaction are better than the ones displayed by monometallic Pd/TiO_2 and Pt/TiO_2 catalysts, achieving T_{50} values of 220, 280 and 300 °C, respectively. In fact, the reaction rate and TOF values show a synergistic effect by the combination of Pt and Pd, which was confirmed by the Pd and Pt interaction with TiO_2, following the order: Pt-Pd/TiO_2 > Pt/TiO_2 > Pd/TiO_2; likewise, the activation energy showed the sequence Pd/TiO_2 > Pt/TiO_2 > Pt-Pd/TiO_2. The Pt, Pd, Pt^{2+} and Pd^{2+} species and the outstanding Brönsted and Lewis acidity type induced the activation of adsorbed oxygen species, which participated in the propane oxidation. In this line, the computational results showed that Pt tends to increase the Brönsted acidity of the interface, thus favoring oxygen adsorption through a dissociative mode. While the bimetallic system presented a unique behavior in that hydrogen (even abstracted from propane) is less bound to the oxidized site; then, a more Lewis acidic site is attained. Interestingly, the predicted Lewis acidity (Pt-Pd/TiO_2 > Pt/TiO_2 > Pd/TiO_2) through hydrogen adsorption energies, for the single oxidized site, exhibited the same trend as that determined for the catalytic activity, suggested as a possible chemical reactivity descriptor for the oxidation of propane. The stronger acidity of the bimetallic system might also improve the catalyst water tolerance compared to monometallic analogue systems.The relatively high surface area of the synthesized TiO_2 with highly reactive bimetallic Pt-Pd nanoparticles did not allow high accumulation of carbonates on the surface of the Pt-Pd/TiO_2 catalyst, displaying moderate thermal stability and resistance to deactivation. Moreover, in-situ DRIFTS characterization revealed that propane was dehydrogenated and then, surface adsorbed oxygen oxidized propane to CO_2 and H_2O on the Pt-Pd/TiO_2 catalyst.

Acknowledgments

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Outstanding synergistic effect of Au-Ir/Al_2O_3 catalysts on the total oxidation of propane

R. Camposeco, R. Zanella*
Instituto de Ciencias Aplicadas y Tecnología, Universidad Nacional Autónoma de México, C. U., 04510, Ciudad de México, Mexico
**rodolfo.zanella@icat.unam.mx*

Introduction. Volatile organic compounds (VOCs) are emissions generally coming from industrial processes and transport. There are two types of catalysts that can be used to eliminate VOCs: noble metals supported on oxides and metal oxides mainly supported on TiO_2, Al_2O_3, and SiO_2. Earlier studies have evidenced that Pt/Al_2O_3 presents activity in the catalytic oxidation of toluene and propene, likewise, it has been reported that γ-Al_2O_3 possesses specific surface properties that allow the achievement of good dispersion (up to 70%) of metallic active phases. Previous studies have reported that iridium atoms donate electrons with more facility than gold atoms when both metal atoms interact as nanoparticles; this interaction can modify the capability of gold to donate electrons. However, Au-Ir has not been reported as a catalytic system for the total oxidation of propane. Inspired by the previously mentioned and because gold catalysts are not stable in the total oxidation of C_3H_8, Au/Al_2O_3, Ir/Al_2O_3 and bimetallic Au-Ir/Al_2O_3 catalysts were synthesized and approached from the highlights of metal loading, dispersion, gold and iridium species on the catalyst surface and their adsorption capacity, as well as their surface acidity type.

Experimental/methodology. The synthesis of γ-Al_2O_3 was performed by the sol-gel method. Au/Al_2O_3, Ir/Al_2O_3 and bimetallic Au-Ir/Al_2O_3 catalysts were synthesized by the deposition precipitation with urea metod. A sequential deposition of iridium and gold on Al_2O_3 was carried out for the bimetallic samples. The synthesized materials were characterized by XRD, HRTEM-HAADF, H_2-TPR, UV-vis, and pyridine thermo-desorption, followed by FTIR and XPS, showing distinct characteristics that were correlated with their catalytic activity. The catalytic activity was evaluated by temperature programmed experiments using a flow reactor at atmospheric pressure. Flow mass controllers were used to set the flow of a gas mixture at 5000 ppm of C_3H_8 and 2% of O_2 in N_2 with a total flow rate of 100 mL min^{-1}. CO_2 concentration in the effluent gas was monitored online using a gas chromatograph Agilent Technologies system equipped with a methanizer

Results and discussion.

The monometallic Ir/Al_2O_3 catalysts turned out more active than the Au/Al_2O_3 ones. The addition of iridium to Al_2O_3 suppressed the crystal growth, resulting in more defects on its surface and high surface area. The superior performance of the Ir/Al_2O_3 catalysts may be associated with Ir^{2+} species, oxygen vacancies and adsorption oxygen sites on their surface. The bimetallic materials displayed outstanding synergistic performance in the propane oxidation reaction compared to their gold and iridium monometallic counterparts at low reaction temperatures. Outcomes revealed a strong interaction among the gold and iridium particles when the catalysts are activated in H_2 and that the thermal treatment atmosphere (hydrogen or air) modifies the active sites; likewise, gold–iridium and monometallic iridium catalysts supported on γ-Al_2O_3 showed considerable endurance to activity loss because they hardly presented metal sintering at high reaction temperatures. Moreover, XPS results revealed electron transfer between Au-Ir. Only the bimetallic system presented Lewis and Brönsted acidity, which may have been responsible for enhancing the total oxidation of C_3H_8. The superiority of bimetallic catalysts was confirmed by the use of a GHSV of 41,000 h^{-1} and the addition of 5 vol. % water. Additionally, the 3Au-5Ir/Al_2O_3 catalyst exhibited considerable stability in cycling and long-term stability tests in the C_3H_8 oxidation, setting it as a potential candidate to be used in real VOC removal processes.

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Pd-MeOx/Al_2O_3 (Me= Co or Ni) catalysts for methane combustion

S. Zh. Todorova[1]*, A. I. Naydenov[2], R. H. Velinova[2], Y. G. Karakirova[1], H.G. Kolev[1]

[1] *Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 11,1113 Sofia, Bulgaria*
[2] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 11,1113 Sofia, Bulgaria*
**Corresponding Author: todorova@ic.bas.bg*

Keywords: methane combustion, Pd-MeOx/Al_2O_3 catalysts

Introduction. Catalytic combustion of methane has been extensively investigated for emission control and power generation during the last decades. The alumina-supported palladium catalyst is widely accepted as the most active catalysts for catalytic combustion of methane. The activity of Pd/Al_2O_3 decreases during time on stream, especially under water vapor. The following order of activity in the reaction of complete oxidation of methane was established: Co_3O_4> CuO>NiO> Mn_2O_3> Cr_2O_3 [1]. It may be expected that the combination between Pd and these oxides could lead to the promising catalysts in reaction of complete methane.

Experimental/methodology. In the present work, we investigate the activity of Pd/Al_2O_3 catalysts promoted with metal oxides (MOx; M= Ni and Co). The Pd-based catalysts modified by metal oxide were prepared by sequential impregnation of Al_2O_3 with aqueous solutions of $Me(NO_3)_2.6H_2O$ and $Pd(NO_3)_2.6H_2O$ and next calcination. All samples were characterized by XRD (X-ray diffraction), TPR (temperature-programmed reduction), EPR (electron paramagnetic resonance) and XPS (X-ray photoelectron spectroscopy).

Results and discussion. According to the XRD data finely dispersed palladium particles were formed on the surface of all samples. XPS analysis shou the present ff both Pd^{2+} and Pd^{4+} on the surface of the fresh catalysts modified with Co and Ni only. The EPR data also suggest the existence of Pd^{+} or Pd^{3+} forms on the surface of the monocomponent Pd/Al_2O_3 and the exchange interactions between paramagnetic palladium species and nickel ions in Ni-Pd/Al_2O_3. Concerning Ni, EPR suggests the presence of Ni^{2+} ions located in partly dehydrated $Al(OH)_3$, orthorhombic Ni^{+} species and a Ni^{+} species in axial symmetry. The reduction behavior of the synthesized catalysts was investigated by means of TPR (Figure 2). Several reduction maxima were observed. The hydrogen consumption in the interval 70-103 °C is attributed to the reduction of PdO [2]. The peak at 350 °C in Ni modified catalyst is ascribe to the reduction of finely divided NiO particles [2]. The reduction peaks at 387 and 500 °C in Pd/Co/Al_2O_3 catalysts are ascribed to the two-step reduction of Co_3O_4. The hydrogen consumption above 500 °C in all samples is attributed to the reduction of Ni-Al or Co-Al oxide phases [2, 3].

An improvement of activity was observed after modification with cobalt and oxides. We suggest that occurrence of Co-Al and Ni spinel phases plays a significant role for the stabilization of the palladium as PdO, leading to high activity and stability in methane combustion.The Pd+CoO_x/Al_2O_3 sample demonstrates remarkable stability after ageing thus the Pd/Al_2O_3 catalysts modified with Co exhibit the most promising catalytic activity for methane oxidation.

Acknowledgments

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Fine chemicals

Lecture: Palladium catalysts supported on biodegradable urea-based polymers in synthesis with CO

M. Markovič, P. Lopatka, P. Koóš, T. Gracza, T. Soták, M. Králik

Institute of Organic Chemistry, Catalysis and Petrochemistry, Slovak University of Technology, Bratislava, Slovak Republic
milan.kralik@stuba.sk

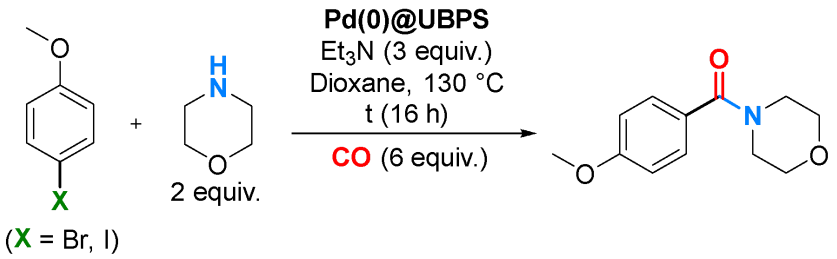
Keywords: urea polymer support, palladium catalyst, microreactor, carbonylation

Introduction.

Palladium supported catalysts belong to the most efficient catalytic systems for the reductive carbonylation, carbonylative reduction and formation of organic carbonates, particularly via cross-coupling reactions [1]. Based on our previous results with homogeneous palladium catalysis [2,3] and activity enhancement by crosslinked supports containing amide groups [4], we have developed new original catalysts using biologically degradable urea polymer supports. The prepared catalysts were tested in the Heck type aminocarbonylation of aryl halide and morpholine.

Experimental/methodology.

Pentamethylene diisocynate trimer (Desmodur® eco N 7300, Covestro), 1,5-pentanediamine (cadaverine, Merck) as a crosslinker and 2-picolylamine (Merck) for derivatizing of NCO groups, were used for the preparation of polymeric support (UBPS). Palladium catalysts (Pd(0)@UBPS) were prepared by the absorption of palladium acetate and its subsequent reduction employing either $NaBH_4$ or H_2 or Et_3N in dioxane. The carbonylation reaction (example is in Scheme 1) was carried out in a two chamber (vial) system using $FeBr_2(CO)_4$ as an *ex-situ* CO source. The NMR, HPLC and GC-FID techniques were used for the analysis of reaction mixtures.



Scheme 1. Carbonylation reaction using the Pd@UBPS catalyst.

Results and discussion.

4-Haloanisoles (bromo- and iodo-) were tested in the carbonylation reaction according to Scheme 1. The best result was obtained using 4-iodoanisole (*IAnis*) and 1 mol % of Pd in the Pd@UBPS catalyst (reduced with Et_3N). The reaction proceeded with 99 % conversion of *IAnis* and (4-methoxyphenyl)(morpholin-4-yl)methanone) was obtained in 96 % isolated yield. Three recycling of the catalyst with a minimum loss of its activity showed the efficiency of this catalyst in the studied carbonylation reaction. The reaction of 4-bromoanisole *(BrAnis*) proceeded only with a low conversion (about 1.5 %), and chloro derivative (*ClAnis*) exhibited virtually zero activity under similar conditions. Achieved results are promising for a facile route to various aroyl amide derivatives – important intermediates for biologically active substances.

Acknowledgments

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Competing commercial catalysts: Unprecedented catalyst activity and stability of Mizoroki-Heck reaction in a continuous packed bed

Nemanja Vucetic[1], Pasi Virtanen[1], Andrey Shchukarev[2], Tapio Salmi[1] and Jyri-Pekka Mikkola[1,2,*]

[1]*Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, 20500 Åbo-Turku, Finland*

[2]*Department of Chemistry, Chemical-Biological Centre, Umeå University, SE-90187 Umeå, Sweden*

[*]*jyri-pekka.mikkola@umu.se; jpmikkol@abo.fi*

Introduction

The growing interest in the production of fine chemicals, pharmaceuticals and agrochemicals by continuous process technology is reflected by several studies found in open literature. The main obstacle for adopting continuous processes as a standard technology for Mizoroki-Heck reaction usually lies in its specific reaction mechanism. Here we present an important step forward answering the challenges unraveled through a comprehensive study that provides deeper understanding on the Mizoroki-Heck reaction, in particular the case when iodobenzene and butyl acrylate react in a continuous packed bed reactor in the presence of a Supported Ionic Liquid Catalyst (SILCA) containing Pd. A simple continuous flow process was proposed resulting in a high catalytic activity (up to 1470 mol_{ArI} $mol_{Pd}^{-1}h^{-1}$) thus competing with the performance of commercial catalysts. For the production of pharmaceuticals, carbon–carbon couplings are very important branch of reactions, often they are the key step in formulating more complex molecules for the synthesis of fine chemicals and active pharmaceutical ingredients (APIs). Nowadays it is widely accepted that the reaction is based on the Pd^0 catalysis and throughout the reaction cycle, palladium alternates between the oxidation states Pd^0 and Pd^{2+}. The real nature of the palladium is more dynamic (the release-and-catch mechanism).

Experimental

A simple packed bed reactor system was designed and used to investigate the catalyst performance in the presence of triethanolamine base. The main goal was minimizing metal leaching and promoting SILCAs as suitable catalysts for C–C coupling reactions in flow. Catalysts with palladium loaded on propyl imidazolium bromidetetramethylguanidinium pentanoate SiO_2 allowed a localised catalytic cycle within the ionic liquid layer. All the experiments were performed in a designed tubular reactor with 0.7 cm internal diameter and 15 cm length. The temperature was monitored with four thermocouples in order to control the temperature in the bottom, middle and top segment of the catalyst bed. The catalyst bed length was 9 cm. Outlet of the reactor was passed throughout the UV–VIS analyzer, while the system of valves allowed collecting GC aliquots before and after reactor and the UV–VIS analyzer.

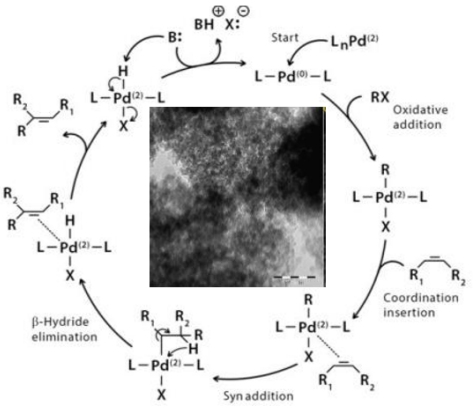

Figure 1. Heck Reaction: Definition, Example, Mechanism, & Application, (n.d.). https://www.chemistrylearner.com/heck-reaction.html (accessed April 2, 2021)

Results and discussion

For studying the Mizoroki-Heck reaction under continuous flow conditions, a simple tubular reactor with 7 mm internal diameter of the tube and 9 cm length of the diluted catalyst bed was applied. Exploring the impact of the individual compounds on the palladium leaching from the catalyst surface in a continuous reactor system unravelled the catalyst stability. Agglomeration can be suppressed with the use of ligands, while in case of pseudo-heterogeneous systems (release-and-catch mechanism) ligandlike species must be permanently anchored to the surface of the catalyst. Thus, the obtained insights together with the information received with ICP-OES, TEM and XPS led to expanded understanding of the catalytic cycle, deactivation mechanism and to the hypothesis that the reaction is proceeding in the ionic liquid layer. All this served to design an efficient continuous process with low Pd loading and leaching, activity as high as 1470 mol_{ArI} mol_{Pd}^{-1h-1}, reaching productivity in the range of 12,000 to 16,000 mol_{ArI} mol_{Pd}^{-1} and competing commercially available catalysts.

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Supported Gold Nanoparticles as Single-Electron Transfer Catalysts for Cross-Coupling Reactions

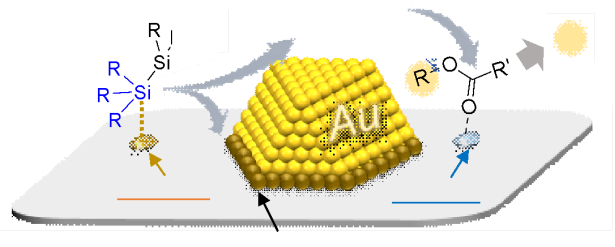
H. Miura[1,2*], M. Doi[1], Y. Yasui[1], K. Ameyama[1], and T. Shishido[1,2]

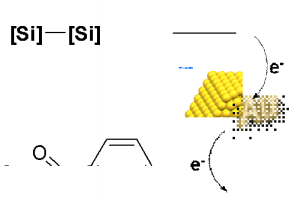
[1]*Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Hachioji, Tokyo, Japan*
[2]*Research Center for Hydrogen Energy-based Society, Tokyo Metropolitan University, Hachioji, Tokyo, Japan*
*miura-hiroki@tmu.ac.jp

Keywords: Gold nanoparticles,cross-coupling, single-electron transfer catalysts

Introduction. Supported gold nanoparticles (Au NPs) exhibit excellent catalytic activity in a wide range of chemical reactions. Detailed studies mainly based on electron paramagnetic resonance (EPR) spectroscopy have revealed the harmonic interaction between Au NPs and organic radicals. These findings led us to reconsider whether several catalytic organic transformations under the influence of Au NPs might include single-electron transfer. In this study, we report that supported Au NPs function as a heterogeneous single-electron transfer catalyst to promote cross-coupling reactions for synthesizing various alkylsilanes[1] and alkyl boronates[1,2].

Results and discussion. Au/ZrO_2 catalyst promoted efficiently the cross-coupling of alkyl acetate with disilanes to give the corresponding alkylsilane in high yield. The heterogeneous Au catalysts were effective for the silylation of $C(sp^3)$–O bonds in various alkyl esters and alkyl ethers to afford the corresponding alkylsilanes. In addition, this reaction could be applied to the upcycling of polyesters, i.e., the degradation of polyester and the synthesis of organosilicon compounds were realized concurrently by the unique catalysis of Au/ZrO_2. Mechanistic studies corroborated the notion that the generation of alkyl radicals is involved in $C(sp^3)$–Si coupling and the cooperation of gold and an acid-base pair on ZrO_2 is responsible for the homolysis of stable $C(sp^3)$–O bonds.[1] On the other hand, Au/C catalysts efficiently catalyzed decarboxylative cross-coupling of *N*-hydroxy phthalimide (NHPI) esters with disilanes to give the corresponding alkylsilane. Furthermore, the Au/C catalyst was also effective for decarboxylative C–B coupling to afford alkyl boronates. A detailed mechanistic investigation revealed that single-electron transfer mediated by supported gold nanoparticles enabled the generation of an alkyl radical and silyl radical, thereby enabling radical cross-coupling.[2]





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A study of the acylation of 1,3-Benzodioxole over ion exchange resins

N. Schiaroli[1*], T. Tabanelli[2], A. Guerrini[3], S. Billi[3], C. Lucarelli[1]

[1]*Dipartimento di Scienza e Alta Tecnologia, Università degli studi dell'Insubria, Via Valleggio 9, Como, Italy*
[2]*Dipartimento di Chimica Industriale "Toso Montanari", Alma Mater Studiorum - Università di Bologna, Viale Risorgimento 4, Bologna, Italy*
[3]*Endura S.p.a., Via Pietramellara 5, Bologna, Italy*
[*]*nicola.schiaroli@uninsubria.it*

Introduction. Acylation reactions play an important role in fine chemical industries [1] and are tradionally carried out using inorganic compounds such as $AlCl_3$, $ZnCl_2$ and BF_3, posing serious environmental and economic issues [2]. Thus, the development of heterogenous catalysts able to replace these compounds is of paramount importance. Starting from these premises, in the present work, the potential utilization of different Ion exchange resins as catalysts for the acylation of 1,3-benzodioxole (MDB) to 3,4-Methylenedioxypropiophenone (MDP1P, used in drugs and insecticides) were investigated.
Experimental/methodology. The reactions were carried out in a round 2-neck flask connected to a reflux condenser. The reagent mixture (with no solvent) together with the catalyst were heated to the reaction temperature under stirring and maintained at this temperature for 1 h. The products were analyzed by GC and identified through GC-MS tecnique. The characterization of the catalyst before and after reaction was carried out using SEM, IR, BJH and TG analyses.
Results and discussion. The acylation of MDB, using propionic anhydride (AP) as acylating agent, over acid macroreticular-type resins such as Purolite and Amberlite, showed that the best results in terms of MDP1P yield and selectivity were achieved at 120°C, hitting yields of ≈ 45% but with a high by-products formation. Conversly, Aquivion PW-87 (a perfluorosulfonic acid/gel-type resin) can efficiently catalyze the reaction at 80°C, showing a higher MDB conversion (53%) and a MDP1P selectivity of 79% (Figure 1a). The overall efficiency can be futher boosted by encapsulating the resin into a SiO_2 matrix via a one-pot, sol gel synthesis. Moreover, It was found that, although the PW87/SiO_2 ratio drives the MDB and AP conversion, the yields in by-products can be nearly halved using the new composite.

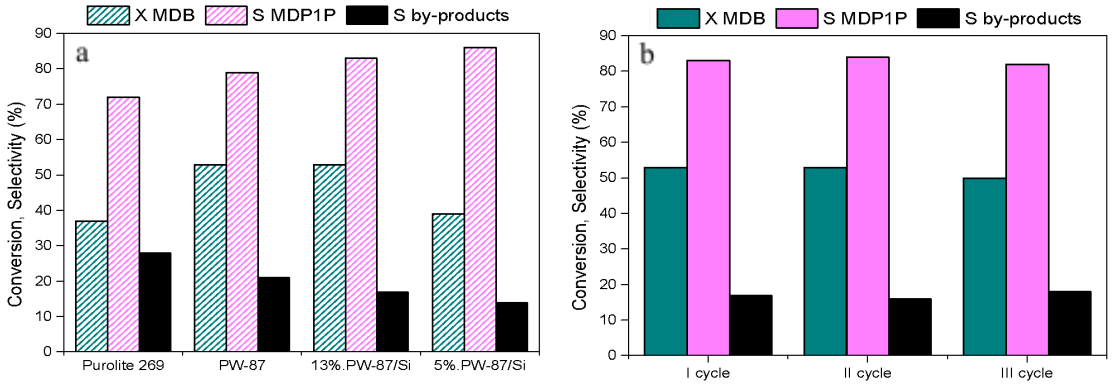

Figure 1: a) catalyst activity in terms of MDB conversion (X), MDP1P and By-products selectivity (S) and b) catalytic activity of 13%.PW-87/Si after each regerenation step with 20% HNO_3 (aq). Reaction conditions: 80°C, 500 rpm, MDB:AP = 1 mol/mol, 1h, mol H^+/ mol MDB = 0.007.

The study of the catalyst deactivation, revealed that the transformation of AP into heavier compounds over the catalyst surface is the main phenomenon that led to the blockage of the active sites during reaction. The regeneration of the resin can be obtained through a fast oxidation of the catalyst surface using an aqueous solution of HNO_3 (20%) or H_2O_2 (20%) at 100°C. In this way, after drying, the PW87-based catalysts can be efficiently reused for several cycles (Figure 1b) without significant activity drops.

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[MnBr(CO)$_5$] as a Precatalyst for the Selective Oxidation of Silanes into Silanols with Water

Emanuele Antico[1,2], Markus Leutzsch[3], Niklas Wessel[1,2], Thomas Weyhermüller[1], Christophe Werlé[1,4] and Walter Leitner[1,2]

[1] *Max-Planck-Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany.*
[2] *Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Aachen, Germany.*
[3] *Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany.*
[4] *Ruhr University Bochum, Bochum, Germany*
**christophe.werle@cec.mpg.de, *walter.leitner@cec.mpg.de*

Keywords: Homogeneous catalysis, manganese, hydrogen, silanols, water, mechanistic studies.

Introduction. Silanols have many applications, ranging from materials science and polymers[1] to medicinal chemistry.[2] Traditional procedures to synthesize silanols proceed via the wasteful hydrolysis of chloro- or alkoxysilanes with a stoichiometric amount of base, consequentially generating stoichiometric amounts of waste.[3] An appealing alternative resides in the oxidation of silanes using H_2O as a green oxidant: hydrogen is produced as the only valuable byproduct, but the reaction often shows significant selectivity issues.

Results and discussion. Herein, we present [MnBr(CO)$_5$] as a highly active and selective precatalyst for this reaction.[4] To our knowledge, this constitutes the first example of using manganese for this specific reaction. [MnBr(CO)$_5$] operates under neutral conditions and avoids the undesired formation of siloxanes (a standard limitation of this reaction). A broad scope of silanols was synthesized in yields up to 98%. The scope includes silanediols and silanols bearing unsaturated functionalities such as allyl- or vinyl-, that can have potential applications in the synthesis of Si-based polymeric materials and are incompatible with traditional synthetic procedures. Moreover, the activation of the Si–H bonds by [MnBr(CO)$_5$] was elucidated studying the reaction kinetics on $PhMe_2SiH$ as a model substrate (including KIEs of $PhMe_2SiD$ and D_2O). The initial activation of [MnBr(CO)$_5$] was clarified, and the experimental data are most consistent with a catalytic cycle comprising a cationic tricarbonyl Mn(I) unit as the active framework. Altogether, these insights offer some catalyst design criteria for future catalytic systems capable of activating σ-bonds (such as Si–H, B–H, and H–H bonds) based on the widely available and earth-abundant manganese.

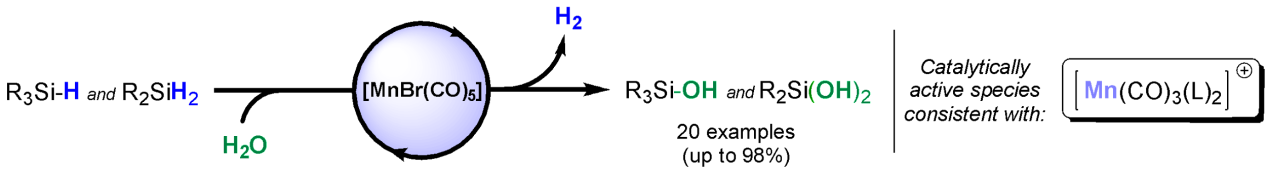

Figure 1: Schematic representation of the work, including the plausible active species mediating the catalytic cycle

Experimental/methodology. Several spectroscopic techniques (FT-IR, ^{1}H-, ^{29}Si-, ^{13}C-, and ^{19}F-NMR), Single crystal XRD, and GC-TCD were used to study the activation mechanism of the [MnBr(CO)$_5$] in the presence of silanes and to perform the kinetic studies used in the elucidation of the overall reaction mechanism. ^{1}H-, ^{29}Si-, ^{13}C-, and ^{19}F-NMR were also utilized to determine the nature and purity of the obtained products.

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Transaminase-membrane reactor for intensified chiral amines synthesis

Hippolyte Meersseman[1*], Tom Leyssens[1], Patricia Luis[1], Francesca Paradisi[2], Damien P. Debecker[1]

[1] *UCLouvain, Louvain-La-Neuve, Belgium*
[2] *University of Bern, Bern, Switzerland*
[*] hippolyte.meersseman@uclouvain.be

Introduction. Chiral amines are essential building blocks for the pharmaceutical industry. Their synthesis often involves multi-step processes requiring costly organometallic homogeneous catalysts [1]. Amine transaminases (ATAs) may provide greener routes to produce chiral amines with excellent enantioselectivity. Yet, industrial applications of ATAs remain restricted to batch processes in which ATAs are employed as free enzymes (non-reusable). One can thus design more versatile heterogeneous biocatalysts able to operate in flow, by immobilizing ATAs on solid supports [2]. Importantly, most targeted transaminations are limited by unfavourable thermodynamics. One strategy to shift the equilibrium towards high chiral amine yields, is the set-up of combined reaction-purification processes. Hence, coupling transaminases with membrane technology in an enzyme membrane reactor is of particular interest, as it could allow the removal of products during operation.

Experimental/methodology. As a proof of concept, we present the immobilization of an ATA from *Halomonas elongata* (HeWT) onto polypropylene (PP) and polyacrylonitrile (PAN) membranes and its application to catalyze the enantioselective synthesis of a model chiral amine in batch (**Fig. 1**). Briefly, PAN surface was chemically modified and coated with polyethyleneimine (PEI) to attract HeWT *via* electrostatic interactions. Glutaraldehyde (GA) was then used to cross-link the loosely attached HeWT and prevent their leaching from the membrane surface. On PP membranes, a covalent grafting strategy was adopted. PP surface was coated with polydopamine (PD) which provided amine functions for further functionalization. The subsequent addition of glycerol diglycidyl ether (GDE) enabled a strong grafting of the enzyme, especially when it was partially derivatized with PEI prior to immobilization.

Results and discussion. The obtained heterogenized ATAs are robust and recyclable, as they successfully performed successive catalytic cycles without deactivation, and with negligeable leaching (as confirmed by hot filtration test). They also showed good (30 %) activity recovery and enhanced stability compared to their soluble counterparts. Thus, we demonstrate the use of novel immobilized ATA carrier materials well-suited for upcoming flow operations, paving the way to intensified processes for chiral amines production.

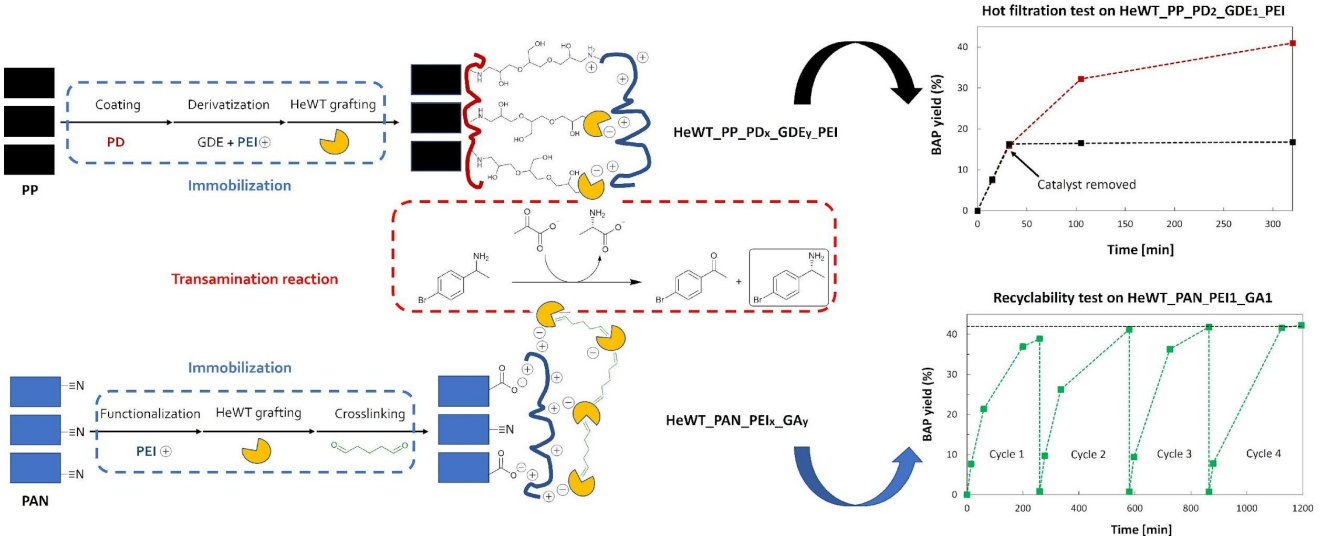

Fig. 1. Left: Representation of the HeWT immobilization procedure on PP and PAN, and of the studied transamination. Right: Hot filtration and recyclability tests of the obtained heterogeneous biocatalysts.

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NENU-5 as precursor of Mo_2C for the syntheis of Anilines

A. Ortega Trigueros[1], D. Villalgordo Hernández[1], I. Such Bañez[2], J. Juan Juan[2], C. Marini[3], E.V. Ramos Fernández[1], M. Caccia[4], J. Narciso[1*]

[1]Institute of Materials(IUMA), Inorganic Chemistry Department, University of Alicante, Alicante, Spain
[2]Technical Research Services (SSTTI), University of Alicante, Alicante, Spain
[3]CELLS-ALBA Synchrotron, Barcelona, Spain
[4]Montana Tech, Butte, Montana, USA
[*]narciso@ua.es

Keywords: NENU-5, Mo_2C, Hydrogenation of nitroarenes

Introduction.

Functionalized anilines are widely used in the Chemical Industry such as pharmaceuticals or cosmetics. To obtain it, perhaps the most efficient route for the preparation of aniline is the reduction of nitroarenes. Currently, the industrial process continues to be non-catalytic, which is inefficient in addition to generating a large amount of waste. Therefore, it is necessary to look for new synthesis routes that are more efficient and friendly to the environment. For this reason, there is currently intense research into the development of efficient and highly selective catalysts for said reaction. An appropriate catalyst is Pt supported on activated carbon, however it has just been reported that Mo_2C based catalysts are also very efficient, especially those obtained by reactive infiltration [1].

The present investigation develops a new Mo_2C that is 10 times more efficient than any Mo_2C reported to date, for this we rely on the modification of HKUST, which is modified by the inclusion in its structure of Mo polyoxometalate cluster, better known as NENU-5

Experimental/methodology.

NENU-5 is treated in different atmospheres from He to He-20% H_2 at temperatures between 500 and 900 ºC depending on the atmosphere used. The material obtained has been characterized by the usual techniques (XRD, XPS, N2 adsorption, SEM, TEM) as well as by more advanced techniques (XANES-EXAFS at ALBA).

For the catalytic tests, the procedure described in [1] has been followed, a theoretical analysis based on the adsorption energy on the different crystalline faces of Mo2C has also been carried out using DFT.

Results and discussion.

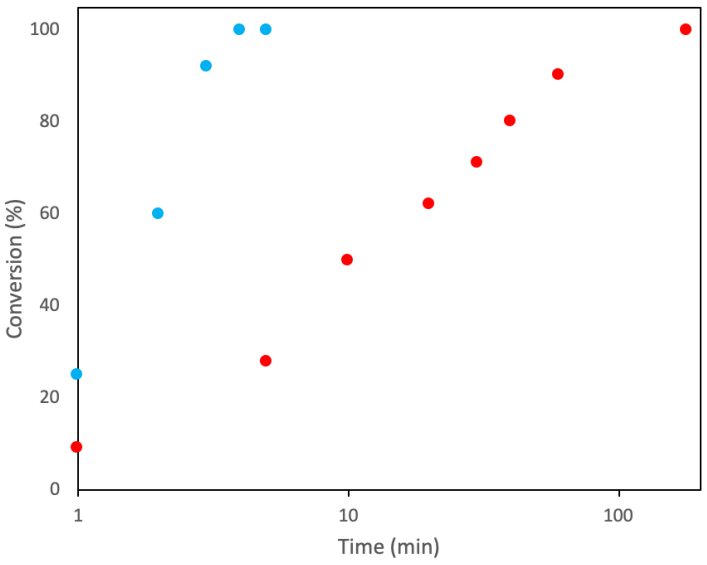

Figure 1 shows the production of para-chloro-aniline as a function of time for one of the catalysts synthesized from NENU-5, and it is compared with the data obtained in [1], as can be seen it is much more efficient, but It is also 100% selective. It is important to point out that said catalyst from the literature already showed results comparable to those obtained by a commercial Pt-C catalyst.

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Figure 1. % conversion of para-chloronitroarene as a function of time (logarithmic).

Florol synthesis via Prins cyclization over hierarchical zeolites of different types and composition

Natalia Shcherban[1,3]*, Roman Barakov[1], Julián E. Sánchez-Velandia[2], Mykhailo Kurmach[1], Oleksiy Shvets[1], Päivi Mäki-Arvela[3], Dmitry Yu. Murzin[3]

[1]*L.V. Pisarzhevsky Institute of Physical Chemistry NASU, Kyiv, Ukraine*
[2] *Jaume University I, Castello de la Plana, Spain*
[3]*Åbo Akademi University, Turku/Åbo, Finland*
[*]*nataliyalisenko@ukr.net*

Keywords: hierarchical zeolite, Prins cyclisation, tetrahydropyranol, Florol, acid sites

Introduction

Hierarchical zeolites are one of the most perspective acidic catalytic materials consisting of a crystalline network that possesses not only uniform micropores, but also secondary meso- or macro-porosity, enabling transformations of bulky organic molecules [1]. The Prins cyclization reaction between biomass-derived isoprenol and isovaleraldehyde results in a commercial perfume ingredient (Florol®) [2]. Besides the desired tetrahydropyranol (THP), this reaction can also give several dehydration products (DHP) (Figure 1) capable of subsequent reactions with the initial substrates (IVA or IP) resulting in trimers.

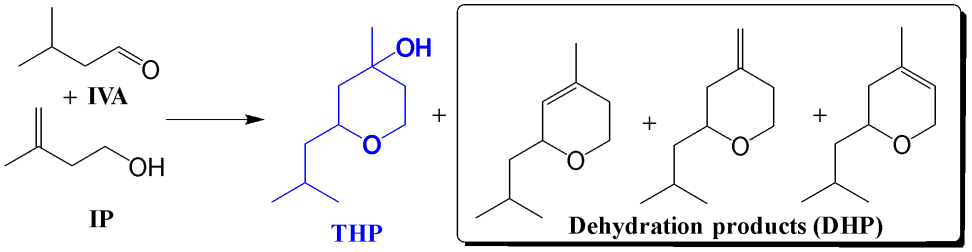

Fig. 1. Prins cyclization of isovaleraldehyde (IVA) and isoprenol (IP) resulting in tetrahydropyranol (2-isobutyl-4-methyl-tetrahydro-2H-pyran-4-ol, THP) and side dehydration products (DHP).

Specifically, this work was devoted to the investigation of the influence of textural and acidic properties of synthesized hierarchical beta zeolites on their catalytic activity in the Prins cyclization of isovaleraldehyde with isoprenol. Due to the presence of mesopores in the hierarchical zeolites mitigating steric limitations in converting bulky molecules exceeding the zeolite micropore size and enhancing the intracrystalline diffusion, these materials can be promising catalysts in the Prins cyclization of isovaleraldehyde with isoprenol.

Experimental/methodology

In this work, Prins cyclization of isoprenol with isovaleraldehyde was carried out in the liquid phase using a batch-mode operated glass reactor at mild reaction conditions (40 °C, atmospheric pressure). A set of hierarchical beta zeolites prepared from a concentrated alkali metal-free protic acid-containing zeolite gel-precursor, as well as Al-, Ga-, Fe-, B-silicate hierarchical zeolites of various structures (BEA, MOR, MFI, FER) and morphologies (nanoparticles, nanosheets or nanorods) was applied for catalysis.

Results and discussion

Among Beta zeolites prepared from concentrated reaction mixtures, the highest yield of the desired product (55.4%) was achieved over a catalyst possessing moderate acidity, developed mesoporosity (V_{meso} 0.60 cm^3/g) and a high external surface area (290 m^2/g). Application of isomorphously substituted samples (with Ga, B) exhibiting a lower strength of acid sites contributes to an increase in selectivity towards the desired product. Catalytic results on Prins cyclization of isovaleraldehyde and isoprenol over the prepared hierarchical zeolites will be presented, showing a clear relationship between the structure and catalytic activity.

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Continuous - flow selective hydrogenation processes towards the formation of pharmaceutical intermediates

Bartosz Zawadzki[1], Rahma Abid[1], Jaroslav Kocik[2], Mirosław Krawczyk[1], Dmytro Lisovystkiy[1], Grzegorz Słowik[3], Krzysztof Matus[4], Wojciech Patkowski[5], Wioletta Raróg – Pilecka[5], Anna Śrębowata[1]*

[1]*Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland*
[2]*ORLEN UniCRE a.s., Litvínov, Czech Republic*
[3]*Maria Curie-Skłodowska University, Lublin, Poland*
[4]*Silesian University of Technology, Gliwice, Poland*
[5]*Warsaw University of Technology, Warsaw, Poland*
[*]*asrebowata@ichf.edu.pl*

Keywords: continuous-flow hydrogenation, 2-methyl-3-butyn-2-ol, 2-butyne-1,4-diol, 2-methyl-2-pentenal, transition metal catalysts

Introduction. Sustainable development requires modern, more intense, more efficient, and environmentally friendly technologies [1]. Implementing the liquid phase continuous-flow operation instead of batch mode belongs to this trend [2]. In particular, it seems to be important in such a demanding field as the pharmaceutical industry, which focuses on achieving 100% selectivity for the desired product. Therefore the primary goal of the studies was to create a relationship between the structure of the readily available 3d transition metal catalysts and their reactivity in continuous-flow hydrogenation of the precursors of relevance to the pharmaceutical industries [3]. In our studies, the continuous-flow mode was successfully implemented, e.g. for semi-hydrogenation of 2-methyl-3-butyn-2-ol and 2-butyne-1,4-diol towards forming essential A, E and B6 vitamins intermediates, several insecticides and antitumoral chemicals. Chemoselective hydrogenation of 2-methyl-2-pentenal led to the formation of two desired products: 2-methylpentanal: an essential intermediate for dyes, resins and drugs production or 2-methylpenten1-ol: valued in perfume production.

Experimental/methodology. 6 wt% Cu catalysts were synthesized by different methods (grafting on the polymeric resin (TS-NH_2), simple impregnation (active carbon supported catalysts), or precipitation in the case of hydrotalcite derived materials). The liquid-phase catalytic selective hydrogenation was performed in the temperature range from 10 to 100°C and pressure range from 1 to 60 bar, using continuous-flow microreactor with an HPLC pump. The proper interpretation of the catalytic results was supported by physicochemical characterization using physisorption analysis, TGA, ICP OES, TPR, H_2-TPD, NH_3-TPD, CO_2-TPD, XRD, including XPS, in-situ TEM measurements and by DFT calculations.

Results and discussion. Our results show that catalysts containing small Cu content are active and stable in selective hydrogenation processes toward forming industrially relevant chemicals (2-methyl-3-buten-2-ol, 2-butene-1,4-diol, 2-methylpentanal and 2-methylpenten1-ol, respectively). Depending on the reaction conditions was possible to obtain high activity and ~ 100% selectivity towards desired products. The selectivity control, while maintaining a high substrate conversion at parameters optimal from an economic point of view, was possible thanks to the synthesis of the catalysts with the specific electronic properties, the presence or absence of the electrophilic sites and the steric effect.

Acknowledgments
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Hydrogenation of *N*-heteroaromatics over SiO_2-supported Ni–Ir alloy catalyst

Masazumi Tamura[1*], Yoshinao Nakagawa[2], Keiichi Tomishige[2*]

[1] *Osaka Metropolitan University, Osaka, Japan*
[2]*Tohoku University, Sendai, Japan*
[*]*mtamura@omu.ac.jp; tomishige@tohoku.ac.jp*

Keywords: Hydrogenation, Alloy catalyst, Heteroaromatics

Introduction. Aliphatic cyclic amines are important chemicals for the synthesis of fine chemicals, pharmaceuticals and pesticides and so on, and they can be synthesized by hydrogenation of *N*-heteroaromatics with hydrogen. Hydrogenation of *N*-heteroaromatics such as pyridines and quinolines is generally difficult because the N atom of the substrates is strongly coordinated to the active metal center of catalysts. Various heterogeneous catalysts have been intensively developed [1]. Supported noble-metal catalysts such as Rh, Pd, Ru and Pt catalysts are typically more active for hydrogenation of *N*-heteroaromatics than the non-noble-metal ones, and Ir is less active among noble metals. Therefore, active non-noble metal-based catalysts are desired to be developed. In our previous works [2], we found that SiO_2-supported Ni-Ir alloy catalyst showed high activity for the hydrogenation of olefins. In this work, we applied the catalyst to the hydrogenation of *N*-heteroaromatics and found that SiO_2-supported Ni-Ir alloy showed high activity for the reaction [3].

Experimental/methodology. Ni-Ir/SiO_2 was prepared by sequential impregnation method. Ir/SiO_2 was synthesized by impregnating SiO_2 with H_2IrCl_6aq, and it was dried at 373 K overnight after removal of water by evaporation at 353 K. Ni was loaded on the Ir/SiO_2 by impregnating Ir/SiO_2 with $Ni(NO_3)_2$aq, followed by drying at 373 K overnight after removal of water by evaporation at 353 K. Finally, the obtained dried Ni-Ir/SiO_2 was calcined at 773 K for 3 h. Activity tests were conducted in a 190-ml autoclave with an inserted glass vessel. The reduced catalyst, a spinner and a mixture of pyridine and methanol were added to the glass vessel in the autoclave. After flashing air in the autoclave by H_2, the reactor was pressured to 1 MPa by H_2 at rt. Then, the autoclave was heated to 353 K and H_2 pressure was increased to 8 MPa.

Results and discussion. Fig. 1 shows the result of catalyst screening of M–Ir/SiO_2 (M=Fe, Co, Ni and Cu, M/Ir=1) and Ni–M'/SiO_2 (M'=Pd, Ru and Pt, Ni/M'=1) catalysts in hydrogenation of pyridine to piperidine as a model reaction. Ni-Ir/SiO_2 clearly showed high activity for the reaction, and other combinations were not effective. Ir/SiO_2 and Ni/SiO_2 also showed low activity. The activity based on the catalyst amount is about 16-fold higher than monometallic Ir and Ni catalysts. Therefore, the combination of Ni and Ir was effective for the reaction. Based on the characterization of Ni-Ir/SiO_2, Ni-Ir/SiO_2 has Ni-Ir alloy, which will be responsible for the high activity. The catalyst was applicable to the hydrogenation of other pyridines and quinolines.

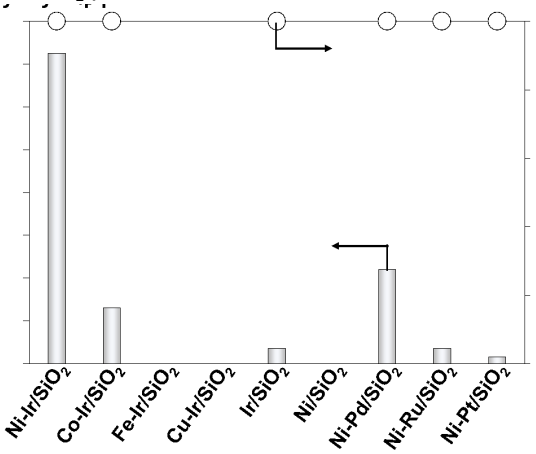

Fig. 1. Catalyst screening of M–Ir/SiO_2 and Ni–M'/SiO_2 catalysts in the hydrogenation of pyridine
Reaction conditions: 0.02 g catalyst (noble metal: 4 wt%), 5 mmol pyridine, 3 g methanol, 8 MPa H_2, 353 K, 4 h.

Acknowledgments
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One-step Basic-catalyzed Double Substitution for the Synthesis of Fused Ring Compound: 3,8-Dibromo-2,9-dinitro-5,6-dihydrodiimidazo[1,2-a:2', 1'-c]pyrazine

Y. X. Liu[1], Z. W. Ye[1*]

[1]*Nanjing University of Science and Technology, Nanjing, China*
[*]*yezw@njust.edu.cn*

Keywords: basic catalysis, double substitution, fused ring compound

Introduction

Energetic materials used in the military field have attracted the interest of scientists worldwide over the past decades as important materials for the development of the weapons industry[1-3]. However, traditional energetic materials no longer met the requirements of rapidly evolving weapons. Compared to conventional energetic materials, fused ring compounds meet the high stability requirements of new energetic materials[4].4,4'-5,5'-tetranitro-2,2'-biimidazole (TNBI)[5] is a member of the common energetic materials. Its high impact sensitivity (IS: 5-6 J) makes it impossible to apply directly. The addition of alkyl groups to synthesize fused ring compounds can result in reduced susceptibility and improved safety.

Experimental section.

4,4'-5,5'-tetranitro-2,2'-biimidazole was used as a raw material and reacted in toluene at high temperature for 48 hours with Na_2CO_3 as a basic catalyst and 1,2-dibromoethane as a reactive agent. At the end of the reaction, the reaction mixture was cooled to room temperature and poured into ice water. The solid product was filtered out and rinsed with plenty of deionized water. The resulting solid dried in the air.

Results and discussion.

The modification of the sensitive 4,4'-5,5'-tetranitro-2,2'-biimidazole (TNBI) was catalyzed by the basic catalyst Na_2CO_3 and the introduction of the alkyl group with 1,2-dibromoethane, which reduces their mechanical sensitivity resulting in a thick ring product with IS > 40J.

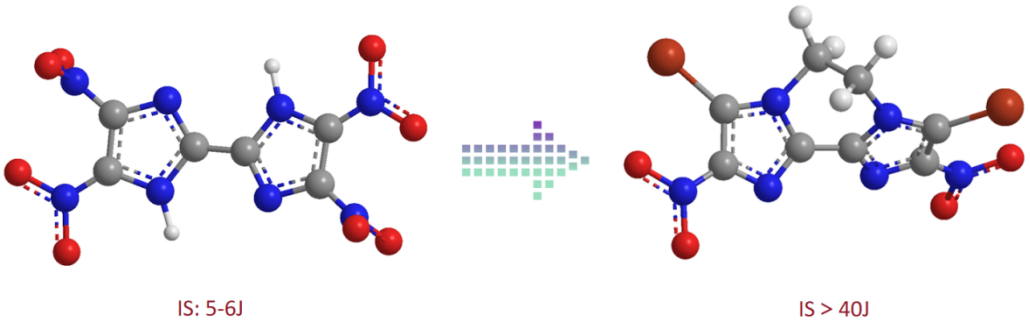

Figure Model of 3,8-Dibromo-2,9-dinitro-5,6-dihydrodiimidazo[1,2-a:2',1'-c]pyrazinee

Acknowledgments

The careful guidance of Professor Zhiwen Ye made this successful synthesis possible!

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Regioselective N-Alkylation of 2-Amino-Azoles with Alcohols for the synthesis of 2-N-(alkylamino)azoles Catalyzed by a Ruthenium Complex Bearing a Functional Ligand

Xiangchao Xu, Yawen Tang, Jin Zhang, Feng Li*

Nanjing University of Science & Technology, Nanjing 210094, P. R. China
**E-mail address: fengli@njust.edu.cn (F. Li)*

Keywords: Regioselective, 2-N-(alkylamino)azoles, Ruthenium complex, Functional ligand.

Introduction. 2-N-(alkylamino)azoles represent a class of important N-containing heterocycles, which display a wide spectrum of biological activities.

Recently, considerable attention has been directed to the N-alkylation of amines with alcohols as alkylating agents based on hydrogen autotransfer process or hydrogen-borrowing strategy,[1] using Ir,[2] Ru,[3] and Pd[4] complexes. As a continuing effort in this field, we wish to describe our effort toward ruthenium-catalyzed regioselective N-alkylation of 2-amino-azoles with alcohols for the synthesis of 2-N-(alkylamino)azoles.

Experimental/methodology. To an oven-dried 25 mL Schlenk tube were added 2-amino-azoles (1 mmol), alcohol (1.2 mmol), catal (0.005 mmol, 0.5 mol %), base (1 mmol, 1 equiv) and *tert*-amyl alcohol (1 mL). The mixture of reaction was heated under 120 °C in an oil bath for 12 h. The reaction mixture was cooled to ambient temperature, concentrated in vacuo and purified by flash column chromatography with ethyl acetate/hexanes to afford the corresponding product.

Results and discussion. Our initial investigation focused on the N-alkylation of 2-aminobenzothiazole with benzyl alcohol. With the optimal reaction conditions in hand, we examined the scope of reaction with respect to alcohols and 2-amino-azoles (Figure 1). It should be pointed that apart from the desired products 2-N-(alkylamino)azoles, no isomer 3-alkyl-2-iminoazolines were found in all cases.

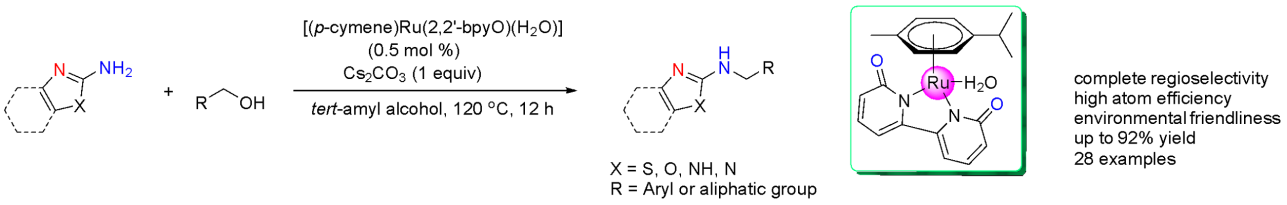

Figure 1. N-Alkylation of 2-amino-azoles with alcohols catalyzed by a ruthenium complex

Based on experimental results, a plausible mechanism is proposed to account for the present regioselective N-alkylation of 2-amino-azole with alcohols. Furthermore, a series of mechanistic experiments were undertaken. To demonstrate the practical potential of the present catalytic system, the gram-scale synthesis of a biologically active molecular was presented.

In summary, we have developed an efficient method for the direct synthesis of 2-N-(alkylamino)-azoles *via* the N-alkylation of 2-amino-azoles with alcohols catalyzed by a ruthenium complex bearing a functional ligand [(p-cymene)Ru(2,2'-bpyO)(H_2O)]. Notably, this study would facilitate the progress of metal-ligand bifunctional catalysts for the hydrogen autotransfer process.

Acknowledgments

Financial support the State Key Laboratory of Fine Chemicals (KF2210) is greatly appreciated.

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Development of a packed bed reactor system for CO_2 hydrogenation to formic acid using ruthenium PNP pincer catalyst

G. Afreen[1], A. Bansode[1], K. Wada[2], M. Hirano[2], H. Matsuda[2], A. Urakawa[1*]

[1]*Catalysis Engineering, Department of Chemical Engineering, Delft University of Technology, Delft, The Netherlands*

[2]*Corporate Research and Development Division, Sustainable Technology Research Center, Nitto Denko Corporation, Osaka, Japan*

[*]*A.Urakawa@tudelft.nl*

Keywords: CO_2 hydrogenation, Packed bed reactor, Homogeneous catalyst, Formic acid

Introduction. The ever-increasing atmospheric concentration of carbon dioxide (CO_2) is a major concern regarding global warming and climate change. Among various strategies to control CO_2 emission into the atmosphere and/or capture CO_2 from the atmosphere, CO_2 utilization to produce C1 chemicals like formic acid (HCOOH) or formate ($HCOO^-$) is an effective approach [1]. Industrially, formic acid is a valuable commodity chemical with uses in preservatives, synthesis precursors, and most notably, as a hydrogen carrier. Its easy decomposition and reversible nature make it an exceptional liquid organic hydrogen carrier (LOHC), capable of storing hydrogen effectively. The process of formic acid formation from CO_2 hydrogenation is an endergonic catalytic reaction making the reaction thermodynamically unfavourable (equation 1) [2].

$$\text{[illegible]}_{2(\text{[illegible]})} + \text{[illegible]}_{2(\text{[illegible]})} \text{[illegible]} \text{[illegible]}_{(\text{[illegible]})} \qquad \Delta\text{[illegible]}^{\circ} = +32.9\ \text{[illegible]}^{-1} \qquad (1)$$

$$\text{[illegible]}_2 + \text{[illegible]}_2 + \text{[illegible]} \text{[illegible]}^{-} + \text{[illegible]}^{+} \qquad \Delta\text{[illegible]}^{\circ} < 0\ \text{[illegible]}^{-1} \qquad (2)$$

Many basic additives such as KOH, $NaHCO_3$, etc are used to promote the reaction and overcome the thermodynamic limitations (equation 2). Another interesting approach is direct reduction of bicarbonate to formate since CO_2 remains in equilibrium with bicarbonate in aqueous medium. Also, bicarbonates are easily formed from CO_2 and alkanol amines. Such hydrogenation reactions have been studied predominantly using homogeneous catalysts such as Ru, Rh, Ir, Co, and Fe complexes in batch reactors under high pressure conditions (~60-100 bar) [3]. However, catalyst recovery and recycle become difficult in such reactor systems.

Experimental/methodology. We have developed a continuous flow packed bed reactor system for effective hydrogenation of bicarbonate premixed with catalyst to form formate using ruthenium PNP pincer organometallic catalyst.

Results and discussion. Under the reaction conditions of 40 bar and at 90 °C, a turnover number (TON) of ca. 4000 was achieved in a single pass, with a formate yield of around 30% (Figure 1). The reaction parameters such as temperature, pressure, residence time, and reactant flow rates are further optimized to improve the TON and yield remarkably. Additionally, the catalyst used in the process can be recovered and recycled for subsequent runs, making the reactor system economically appealing.



Figure 1. Reaction scheme of bicarbonate hydrogenation in a packed bed reactor using Ru PNP pincer catalyst.

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Non-metal doped triazine-based covalent organic frameworks as heterogeneous photocatalysts for biomass conversion

Anise Akhundi*, Michael Wark

Institute of Chemistry, Carl von Ossietzky University Oldenburg, 26129 Oldenburg, Germany

**anise.akhundi@uni-oldenburg.de*

Introduction. Photocatalytic conversion of biomass to fine chemicals is of great importance due to its environmental friendliness and the transformation potential to second generation fuels. 5-hydroxymethyl furfural (HMF) is a biomass-derived key platform molecule to synthesis of fine chemicals [1]. However, developing an efficient metal-free photocatalyst for HMF conversion is a challenging task. In our previous work, exfoliated carbon nitride nanosheets have been prepared by different methodologies and applied for the selective photocatalytic conversion of HMF to 2,5-furandicarboxyaldehyde (FDC) [2]. Now, we deal with synthesis of triazine-containing covalent organic frameworks (COFs) in a microwave-assisted method. We plan to create defects in the structure of the synthesized COFs by doping non-metal phosphorus element. The synthesized defected COFs will be closely characterized by ^{13}C-NMR, FTIR, XRD, elemental analysis, and gas adsorption. The effects of defects on the band gap and energy levels of the photocatalysts will be investigated. The photocatalytic conversion of HMF to 2,5-furandicarboxylic acid (FDCA) will be conducted over the triazine-containing COFs and the activity of photocatalysts in terms of HMF conversion and selectivity towards FDCA will be assessed.

Experimental/methodology. Recently, g-$C_{18}N_3$-COF as a two-domensional triazine-cored COF was solvothermally synthesized upon Knoevenagel condensation using 2,4,6-trimethyl-1,3,5-triazine (TMTA) and 1,4-diformylbenzene (DFB) [3]. Inspired by this study, we use a microwave-assisted method in order to shorten the reaction time and compare the characteristics of the obtained samples with those of others. We plan to improve semiconducting behaviour of triazine-based-COFs by doping with phosphorus. The photocatalytic experiments will be conducted in a quartz glass photoreactor, under irradiation of LED lamps. After a suitable reaction time, the irradiated solutions will be analyzed by HPLC to detect products and possible intermediates of the reaction.

Results and discussion. The main focus of this study is the synthesis of triazine-based covalent organic frameworks, investigation of their physicochemical properties and their application in photocatalytic biomass conversion reactions. Based on our extensive experiences in synthesis and modification of the structure of g-C_3N_4-based nanomaterials [4], we extend similar methodology to synthesis of COFs and their modification via defect-engineering. In our previous work, exfoliation of carbon nitrides resulted in increased specific surface area and improved the conversion of HMF and the selectivity to FDC. Furthermore, achieving P-doped COFs and studying their optical and semiconducting properties is another goal of this research. Our previous study shows (Fig. 1) that phosphorus doping narrows the band gap and extends the light absorption of g-C_3N_4 [5].

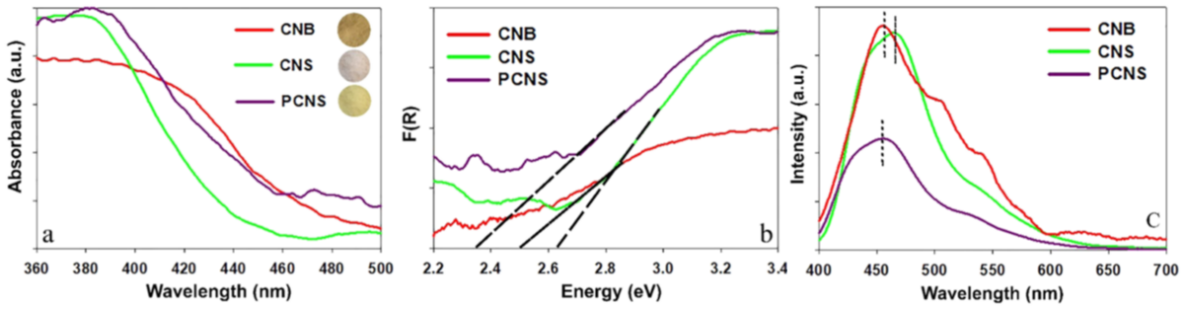

Figure 1. (a) DRS spectra, (b) Tauc plots, and (c) photoluminescence (PL) spectra of bulk g-C_3N_4 (CNB), g-C_3N_4 nanosheets (CNS), and P-doped g-C_3N_4 PCNS

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Reductive amination of levulinic acid to produce pyrrolidones-derived compounds through Nickel Phosphide heterogeneous catalysts.

Araya-López, Claudio[1,2]; Blanco, Elodie[1,2]; Escalona, Néstor[1,2]

1 Departamento de Ingeniería Química y Bioprocesos, Pontificia Universidad Católica de Chile, Santiago, Chile claudio.arayal@uc.cl, neescalona@ing.puc.cl
2 ANID – Millennium Science Initiative Program- Millennium Nuclei on Catalytic Process Towards Sustainable Chemistry (CSC), Chile
**claudio.arayal@uc.cl neescalona@ing.puc.cl*

Keywords: Nickel Phosphide; Reductive Amination; Pyrroldiones

Introduction. There is an abundant amount of biomass on Earth, and it is a promising candidate to replace petrochemical-based compounds. In this line, N-methyl-pyrrolidone (NMP) is an important chemical with a worldwide production of 200-250kton/y, and has been used in petrochemical processes or plastic industry. However, NMP is highly toxic, dangerous and produces infertility and miscarriage. 5-methyl-N-substitute-2-pyrrolidones (5MPs) are an alternative to replace NMP and neither toxic nor cancerous. 5 MPs can be synthesized through reductive amination of levulinic acid plus nitrogen agent using H_2 as reducing agent, also that the levulinic acid can be directly obtained from biomass. This research points out synthesized pyrrolidones-derived compounds through catalytic reductive amination using supported nickel phosphides (Ni_2P) as a heterogeneous catalyst since nickel phosphides have shown promising results hydrogenating organic molecules [1]. **The main objective** is to understand the role of different supports such as SiO_2, ZrO_2 and TiO_2 in the catalytic activity.

Experimental/methodology. a solution of $Ni(NO_3)_2$ and $(NH_4)H_2PO_4$ is put together in acidic water in order to impregnate the support with 10% of Ni and 2:1 P/Ni molar ratio via the incipient wetness impregnation procedure. After leaving the impregnated support mature, this is calcined, reduced under H_2 flow and passivated. The catalyst is characterized by TPD-NH_3, TPR, BET, XRD and XPS. The reaction is carried out in a Parr Reactor using a stoichiometric quantity of levulinic acid and nitrogen agent (Aniline) in dioxane at 200°C and 50bar of H_2 using Ni_2P/SiO_2, Ni_2P/ZrO_2, and Ni_2P/TiO_2, with an atomic density of 3.23 at/nm^2 nominally.

Results and discussion. The preliminary results are shown in **Figure 1**, wherein Ni_2P/SiO_2 and Ni_2P/ZrO_2 do not have a significant difference in the conversion of levulinic acid, but Ni_2P/TiO_2 presented another behavior because it increased the selectivity of molecular intermediaries but not promoting the hydrogenation. The selectivity towards 5-methyl-phenylpyrrolidin-2-one has increased in the following order Ni_2P/TiO_2 < Ni_2P/ZrO_2 < Ni_2P/SiO_2 being oppositely related with the acidity of supports. Additionally, Ni_2P/SiO_2 was compared to Ni/SiO_2, and Ni_2P/SiO_2 suppressed the increase of γ-valerolactone in comparison with the Ni/SiO_2, which promotes the hydrogenation of levulinic acid to γ-valerolactone.

Figure 1: Conversion and selectivity as a function of time

In conclusion, Ni_2P/SiO_2 shows the best selectivity towards pyrrolidone in comparison with the other supports. In contrast, Ni_2P/TiO_2 presents the best conversion because it promotes the production of intermediaries between levulinic acid and aniline.

Acknowledgments
This work was supported by FONDECYT postdoctoral N°3220395, FONDECYT 1220763 and ANID – Millennium Science Initiative Program- Millennium Nuclei on Catalytic Process Towards Sustainable Chemistry (CSC), Chile.

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Atropselective Negishi Coupling at Scale – The Key to an Efficient, Stereoselective Synthesis of GDC-6036

S. Bachmann[1*], R. Bigler[1], U. Orcel[1], E. Trachsel[1], J. Xu[2], H. Zhang[2]

[1] *Process Chemistry & Catalysis, F. Hoffmann-La Roche Ltd., Grenzacherstrasse 124, CH-4070 Basel, Switzerland*

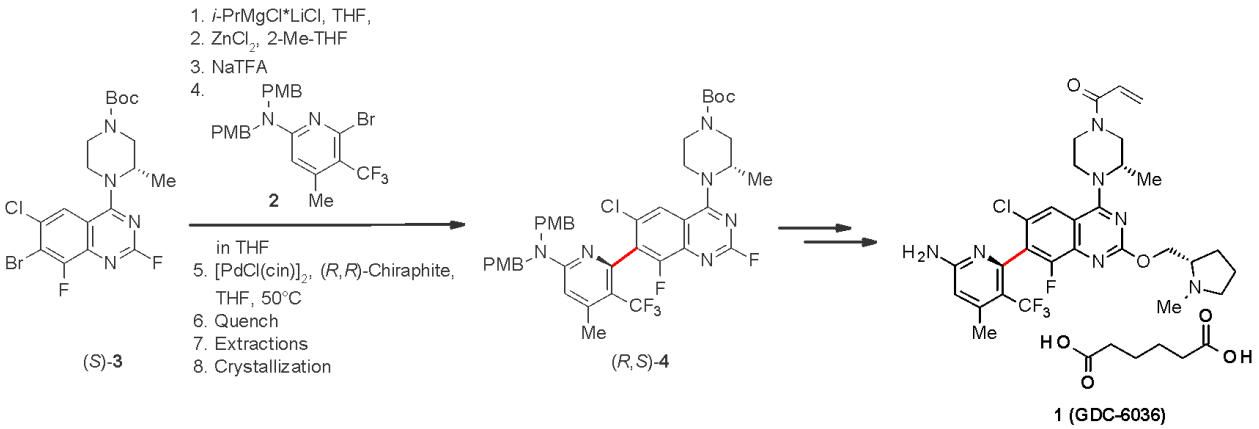
[2] *Small Molecule Process Chemistry, Genentech Inc., 1 DNA Way, South San Francisco, CA 94080, USA*

[*] *stephan.bachmann@roche.com*

Keywords: Catalysis, Atropselective Negishi Coupling, Sustainability, Green Chemistry

Introduction. GDC-6036 (**1**) is a highly potent and selective KRAS G12C irreversible, covalent inhibitor, which is currently in clinical development to treat a wide spectrum of tumors.[1,2] The main synthetic challenge in the synthesis of GDC-6036 (**1**) is the installation of the stereoaxis between the aminopyridine and the quanalozine fragments (bond marked in red in Scheme 1) in a highly selective manner.

Results and discussion. Early R&D efforts applied non-stereoselective approaches, resulting in the need of preparative chromatographic separation techniques to isolate optically pure material.[1] Later, a first stereoselective Negishi coupling of Bromopyridine **2** and the Bromoquanazoline (*S*)-**3** using a Walphos type ligand was identified, giving up to 92% selectivity for the desired (*R*)-atropisomer (*R*,*S*)-**4,** using a ligand that is not commercially available in the required quantities.[2]



Scheme 1: New Pd-catalyzed, atropselective Negishi coupling

Further ligand screening activities identified an unprecedented, highly selective (95% selectivity for (*R*,*S*)-**4**), commercially available and easily accessible ligand (*R*,*R*)-Chiraphite for this transformation.[3] The implementation of this ligand and the identification of an efficient crystallization of (*R*,*S*)-**4** allowed for the development of an economic process for the production of multi hundreds of kilos of GDC-6036. Our efforts and the challenges observed to move this transformation from milligram scale in the laboratory to 125 kg batches in the production plant will be presented.

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Bis(NHC) Mn(I) Complexes: Catalysts for the Hydrogenation of Carboxylic Acid Esters

N. F. Both[1*], A. Spannenberg[1], H. Jiao[1*], K. Junge[1*], M. Beller[1*]

[1]*Leibniz-Institute for Catalysis e.V., Rostock, Germany*
[*]*haijun.jiao@catalysis.de; kathrin.junge@catalysis.de; matthias.beller@catalysis.de*

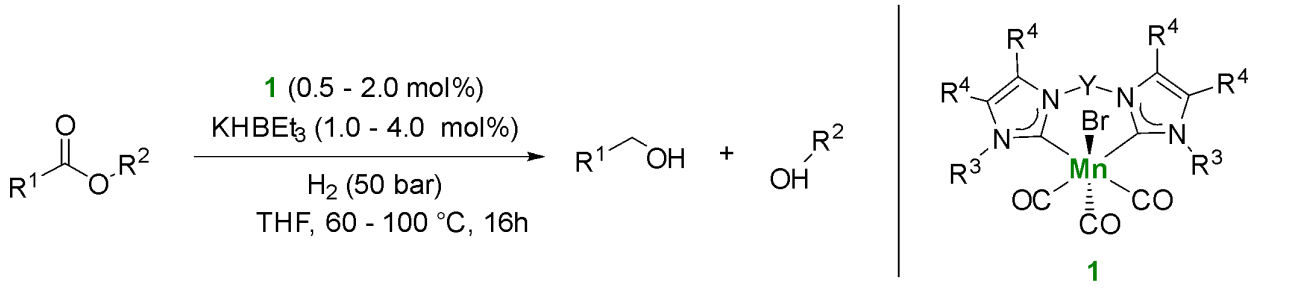
Keywords: Homogeneous Catalysis, Manganese, Carbene Ligands, Hydrogenation, Esters

Introduction. The reduction of carboxylic acid esters to alcohols is an important transformation in academic and industrial chemistry. Therefore, catalytic hydrogenation represents an environmentally and economically attractive approach compared to traditional procedures applying metal-hydrides in stochiometric quantities.

To date, many highly active homogeneous catalysts, mainly based on Ru[1], have been developed which allow for the hydrogenation of carboxylic acid esters at mild conditions. Over the last decade, efforts were made to replace noble metals in such catalysts by more abundant, cheaper, and non-toxic base metals and systems based on Mn, Fe, Co and Cu were reported. Especially Mn[2] has been studied intensely due to the remarkable stability, high activity, and versatility of its pincer complexes. However, the diversity of the known Mn catalysts is very limited since the vast majority relies on phosphine containing ligands including metal ligand cooperative sites. Over the last years it has been shown that also Mn complexes bearing more simple, non-bifunctional ligands can be efficient in hydrogenation-type reactions.[3]

Experimental/methodology. For that purpose, a series of structurally related bis(NHC) Mn(I) complexes **1** were synthesized via a novel synthetic procedure utilizing NHC-borane adducts in very good to excellent yields. Complexes **1** have been characterized by NMR spectroscopy, IR spectroscopy and HR-MS and in two cases additionally by elemental analysis and single crystal XRD.

Results and discussion. Various aromatic and aliphatic carboxylic acid esters have been hydrogenated using complexes **1** with $KHBEt_3$ as cocatalyst under mild reaction conditions (0.5 mol% catalyst loading, 60-100 °C).



Scheme 1: Mn-catalyzed hydrogenation of carboxylic acid esters.

Furthermore, mechanistic experiments reveal the importance of BEt_3 as cocatalyst, which is liberated from $KHBEt_3$ after formation of a hydrido complex. A proposed mechanism is further supported by DFT calculations.

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Enhancing the Chemo-Enzymatic One-Pot Oxidation of Cyclohexane via In Situ H2O2Production over Supported Pd-Based Catalysts

J Brehm[1]*, R. J Lewis[1], X Liu[2] and G.J Hutchings[1]

[1] *Max Planck–Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK*

[2] *School of Chemistry and Chemical, In-situ Centre for Physical Sciences, Frontiers Science Centre for Transformative Molecules, Shanghai, 200240, P.R. China*

** BrehmJJ@cardiff.ac.uk*

Keywords: palladium−zinc, hydrogen peroxide, peroxygenase, oxidation, cascade

Introduction.

Supported Pd-based catalysts have shown to be effective when used in combination with an evolved unspecific peroxygenase from Agrocybe aegerita (PaDa-I variant) to selectively produce cyclohexanol and cyclohexanone (KA Oil) from cyclohexane via in-situ produced H_2O_2, avoiding the by-products typically generated via current industrial approaches. Producing in situ H_2O_2 directly with heterogeneous catalysts overcomes the downsides that incur with other methods; such as the production of unwanted byproducts and atom inefficiency found when coupling with glucose oxidase, or the addition of acid stabilizers or concentration “hot spot” generation that occurs with externally drip fed systems.[1]

Experimental/methodology.

Mono- and bi-metallic 1% Pd-X/TiO_2 catalysts have been prepared via an excess chloride co-impregnation procedure, based on the literature.[2] Cyclohexane oxidation cascade experiments were performed in a one-pot system under conditions conducive to enzyme stability.

Results and discussion.

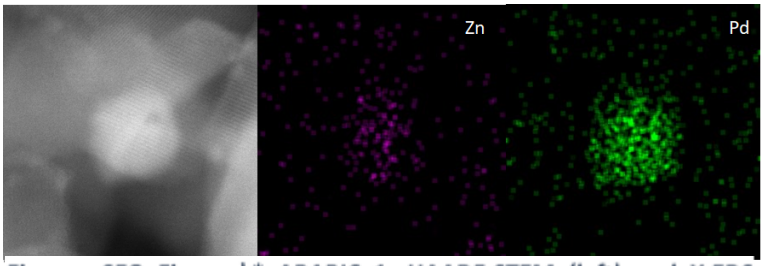

*Figure SEQ Figure * ARABIC 1. HAADF-STEM (left) and X-EDS (purple and green are Zn and Pd respectively) analyses of one of the larger particles showing alloying of the Pd and Zn.*

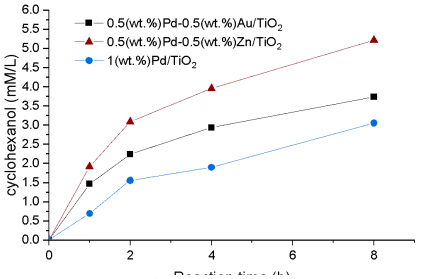

*Figure SEQ Figure * ARABIC 2. Time-on-line of the oxidation of cyclohexane (10mM) to cyclohexanol using Pd based catalysts in cascade with Pada-1*

We have investigated a range of Pd-based catalysts, for the selective oxidation of cyclohexane to KA oil, when used in conjunction with PaDa-I. The alloying of Pd with Zn in particular is found to offer improved catalytic performance compared to PdAu analogues (**Figure 2**), which have been previously reported within the literature.[3] The enhanced activity of the PdZn/TiO_2/PaDa-I system is attributed to the facile formation of PdZn alloys (**Figure 1**) and resulting electronic modification of Pd which offers results in increased selectivity towards H_2O_2 and inhibits chemo-catalyzed over oxidation of cyclohexanol. By comparison, the large population of unalloyed Pd species present in both the PdAu and Pd-only catalysts are found to be responsible for the promotion of further oxidation products and the unselective conversion of H_2O_2 to H_2O, which hampers the overall process efficiency. Additional information can be found at Brehm et al.[4] DOI: https://doi-org.abc.cardiff.ac.uk/10.1021/acscatal.2c0305

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Tandem production of 2-benzimidazole of pharmaceutical interest using Iridium nanoparticles supported onto titanium substituted MCM-41

J. Herrera[1], S. Bedoya[1], D. Gonzalez-Vera[1], C.C. Torrez[2], C.H Campos[1,*]

[1]*Universidad de Concepción, Concepción, Chile*
[2]*Universidad Andres Bello, Sede Concepción, Talcahuano, Chile*
ccampos@udec.cl

Keywords: Tandem reaction, MCM-41, Iridium, 2-benzimidazole.

Introduction: 2-subtituted benzimidazoles are important organic molecules that are building blocks for the preparation of antiviral, anticancer, antiulcer, antihypertensive, antifungal, and antihistamine drugs, among others. Traditionally, these compounds are obtained by two main synthetic routes: (1) through the coupling of o-phenylenediamines with carboxylic acids or their derivatives using conditions that require high temperatures and strong acid conditions or (2) from the transfer reduction/dehydrogenation of 2-nitroaline or o-phenylendiamines with alcohols [1]. Remarkably, non-noble based catalysts demonstrate excellent results in the borrowing hydrogen reduction reaction. Among them, the use of heterogeneous Iridium formulations provides highly efficient and operational stable catalysts for this kind of reaction. However, the effect of the support displayed an important role in the dehydrogenation step [2]. This work is aimed with the effect of iridium nanoparticles (Ir NPs) supported onto titanium substituted MCM-41 structure as catalyst for the tandem production of 2-phenyl-benzimidazole (BZI) – as test reaction – from 2-nitroaniline (2NA) and benzaldehyde (BZ) using Iridium as active phase.

Experimental/methodology. The Ti-substitution onto the MCM-41 structure was carried out according to our previous reported methodology [3]. The obtained solid were prepared with Si/Ti mole as 0, 10, 20, 60 and 120. The deposition of the Ir NPs is carried out using Iridium (III) acetylacetonate precursor (at 0.25 wt%) in acetone as solvent, which was contacted with the and dried in vacuum to obtain the final solid. The solids were calcinated and reduced with H_2. The obtained catalysts were characterized by the following techniques: ICP-MS, H_2-chemisorption, XRD, N_2 adsorption-desorption isotherm, SEM-EDAX, TEM, XPS. The catalytic measurements were carried out in a stainless steel (150 mL) semi-batch Parr-type reactor at 150°C under 5 bar of H_2 pressure for 15 min, then the gas was changed to 5 bar of N_2, using 50 mg of catalyst and 2NA/Ir mole ratio of 100 in cyclohexane as solvent. The reaction products were identified via gas chromatography using a GC Clarus 680 Perkin Elmer instrument equipped with an Rtx-5 Amine column and a flame ionization detector (FID).

Results and discussion. The physicochemical characterization of the Ir supported catalyst displayed a uniform metal dispersion, which increased with the increase of Ti-substitution in the MCM-41 support. In line with these results, the XPS analysis showed an increase in the surface $Ir^{\delta+}$ species with the increase of the metal loading. All the catalyst showed catalytic performance for the preparation of BZI with high selectivity to the target product. Among them, the Ir/MCM-41(Ti20) catalyst displayed the higher catalytic efficiency. Also, this catalyst displayed the optimal operational stability reaching 5 recycles remaining a high conversion and selectivity to BZI production.

Acknowledgments
Agencia Nacional de Investigación y Desarrollo (ANID) FONDECYT Project 1231352 and 1231395. S. Bedoya thanks to University of Concepción EDPG program for his doctoral scholarship.

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Diverse Alkyl–Silyl Cross-Coupling via Homolysis of Unactivated C(sp^3)–O Bonds by Supported Au Catalysts

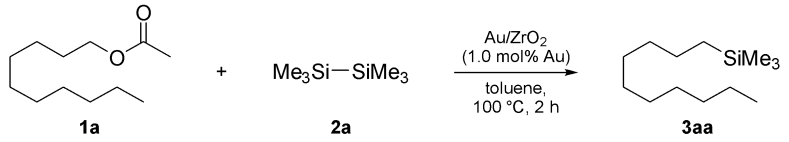
M. Doi[1], Y. Yasui[1], H. Miura[1,2,3*], T. Shishido[1,2,3]

[1]*Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan*
[2]*Research Center for Hydrogen Energy-based Society, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan*
[3]*Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8520, Japan*
[*]miura-hiroki@tmu.ac.jp

Keywords: Gold nanoparticles, C–O bond homolysis, silylation.

Introduction. Since C(sp^3)–O bonds are a ubiquitous chemical motif in both natural and artificial organic molecules, the universal transformation of C(sp^3)–O bonds will be a key technology for achieving carbon neutrality. Generally, sulfonyl and allyl groups, which have activated C(sp^3)–O bonds, have been used for cleaving them. However, the general strategy for enabling alcohols, ethers, and stable esters, as a carbon electrophile to accommodate in cross-coupling reactions remains underdeveloped. Here, we report that supported Au catalysts efficiently generated alkyl radicals via homolysis of C(sp^3)–O bonds, which consequently promoted C(sp^3)–Si bonds formation to furnish diverse organosilicon compounds [1].

Results and discussion. Cross-coupling of decyl acetate (**1a**) with hexamethyldisilane (**2a**) in toluene with 1.0 mol% of Au/ZrO_2 catalyst at 100 °C gave the corresponding alkylsilane (**3**) in 88% yield (Scheme 1).

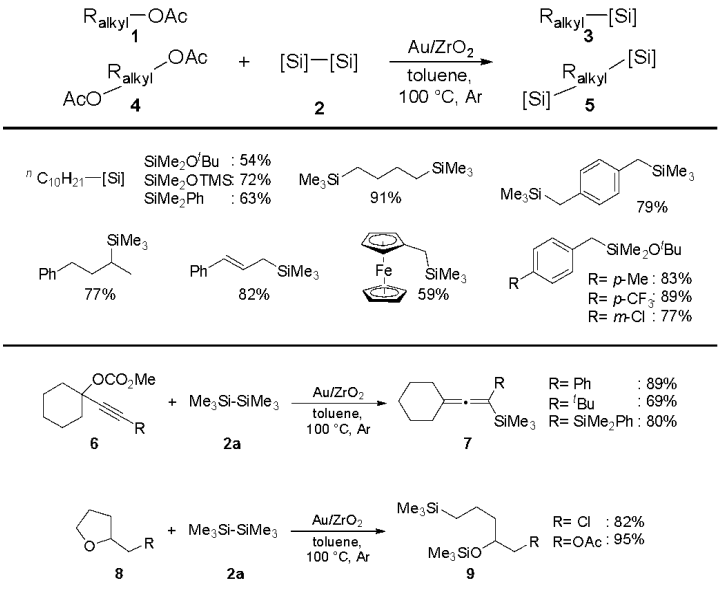


Scheme 1. Au/ZrO_2-catalyzed silylation of C(sp^3)–O bond

With the optimized reaction conditions and catalysts in hand, the scope of the Au-catalyzed C–Si coupling reaction was examined. (Table 1). The reaction of primary and secondary alkyl acetate with a variety of disilanes provided the corresponding alkylsilanes (**3** and **5**) in high yields. The reaction of propargyl carbonate (**6**) also took place to give allenylsilane (**7**) in high yield. Interestingly, Au/ZrO_2 catalysts promoted the ring-opening silylation of cyclic ethers (**8**) to provide alkylsilnaes (**9**).

Mechanistic studies indicated that the homolysis of stable C(sp^3)–O bonds of alkyl esters proceeded to generate alkyl radicals. The cooperation of Au nanoparticles and the amphoteric nature of the support are responsible for the generation of silyl radical and subsequent formation of alkyl radicals, thereby enabling efficient alkyl–silyl coupling to furnish diverse alkylsilanes.

Table 1. Substrate scope of substrates



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One-pot synthesis of 2-substituted benzimidazoles by bimetallic Ni-Co supported onto TiO_2 catalysts

D. González-Vera[1*], J.N. Díaz de León[2], C.C. Torres[3], C.H. Campos[1]

[1]*Universidad de Concepción, Concepción, Chile*
[2]*Universidad Autónoma de México, Ensenada B.C., México*
[2]*Universidad Andres Bello, Sede Concepción, Talcahuano, Chile*
[*]*dagonzalezv@udec.cl*

Keywords: nickel, cobalt, nitroarenes, benzaldehydes, benzimidazoles.

Introduction. Benzimidazole nucleus occupies a prominent position among N-containing heterocycles due to its widespread use in different fields and the number of synthetic methodologies employ for their preparation. Recent trends show that the interest of the scientific community is now bending towards exploring the use of transition metal based heterogeneous catalyst for the synthesis of benzimidazoles [1]. This work is aimed at development a new class of catalytic systems obtained from H_2-assisted reduction of $Ni_xCo_{1-x}TiO_3$ mixed oxides to produce bimetallic Ni_xCo_{1-x}/TiO_2 catalysts (were x = 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0). These systems were tested for the selective hydrogenation of 2-nitroaniline followed by the condensation of o-phenylenediamine with benzaldehyde to provide the corresponding 2-benzimidazole. The optimal catalyst was used for reusability test and the one-pot synthesis of 2-substituted benzimidazoles using 2-nitroaniline and other aldehydes.

Experimental/methodology. The Ni_xCo_{1-x}/TiO_2 catalysts were prepared based in a sol-gel methodology from the $Ni_xCo_{1-x}TiO_3$ mixed oxides as precursor [2]. The obtained precursors and catalysts were characterized by TPR-H_2, XRD, TEM and XPS techniques. The catalytic measurements were carried out in a stainless steel (150 mL) semi-batch Parr-type reactor at 150°C under 10 bar of H_2 pressure for 30 min, then the gas was changed to 5 bar of N_2, using 25 mg of catalyst and the amounts of substrate needed to attain a $mol_{2\text{-nitroaniline}}$:$mol_{metals}$ ratio of 100 in ethyl acetate. The stirring speed was kept at 700 rpm to avoid mass transfer limitations. The reaction products were identified via gas chromatography using a GC Clarus 680 Perkin Elmer instrument equipped with an Rtx-5 Amine column and a flame ionization detector (FID).

Results and discussion. The characterization of the $Ni_xCo_{1-x}TiO_3$ mixed oxides showed a unique reduction temperature between 500-600°C for all systems. The increase of the Ni composition in the as-prepared materials displayed a change in the reduction profile, resulting in a shift to lower temperatures as the nickel content increases. The study of these systems demonstrates that after 5 h of reduction at 550°C all the system produced the corresponding metallic Ni_xCo_{1-x}/TiO_2 catalysts. The XRD results agree with previous result, showing that the bimetallic phase is formed in all the proposed catalysts. TEM micrographs indicates that the mixed oxides precursors possess a nanorods structure and after the reduction treatment the catalyst preserved this shape. The XPS analysis displayed that the Co and Ni metals are almost in zero valent state for all system studied. The catalytic activity showed that all the catalysts were active in the tandem synthesis of 2-benzimidazole and the yield to the target product is function of the Ni content. The most efficient and selective system was $Ni_{0.1}Co_{0.9}/TiO_2$, due to the composition of the bimetallic alloy. Furthermore, $Ni_{0.1}Co_{0.9}/TiO_2$ exhibited a high operational stability in the test reaction reaching 5 catalytic cycles without losing its activity. Finally, the catalytic activity of $Ni_{0.1}Co_{0.9}/TiO_2$ was tested in the one-pot synthesis of 2-substituted benzimidazoles from 2-nitroaniline and aldehydes, showing high activity and selectivity to the desire 2-substituted benzimidazole. The balance of Ni-Co metals in the catalyst's formulation provides an optimal balance in the tandem reactions to produce the target product.

Acknowledgments
The authors thank ANID projects FONDECYT 1231352 (Chile) and 1231395 (Chile). D. González- Vera acknowledges ANID for her PhD fellowship N° 21200167.

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Reactive distillation for continuous production of Ethyl chloro acetate

G.Chhavi[1*], M. Sanjay[2]

[1]*Indian Institute of Technology Bombay, Mumbai,India*
[2]*Indian Institute of Technology Bombay,Mumbai, India*
[*]*gpta.chhavi@gmail.com*

Keywords: Process Intensification, Reactive Distillation, Green engineering

Introduction. Fine chemicals are high-value chemical products with ample potential for advancement in manufacturing processes, especially in process development and green practices. Numerous fine chemicals follow the basic chemistry of esterification reactions, often limited by equilibrium, affecting the final yield[1].Removal of the undesired product in the reaction can push the equilibrium in forward direction. Reactive distillation (RD) is a process intensification technique which could overcome these limitations by providing reaction and separation in a single unit [2]. The scope of this work entails the application of RD for continuous production of Ethyl chloro acetate (ECA), a widely used organic solvent used in pharmaceuticals, plant protection chemicals and heterocyclic compounds production. ECA is produced by the esterification of Mono-chloro acetic acid (MCA) and ethanol (EtOH) in the presence of an acidic catalyst [3]. The catalyst employed in this study is amberlyst-15, an ion exchange resin which can be reused for multiple reaction runs, thus minimizing the neutralizing and separation requirements [4].

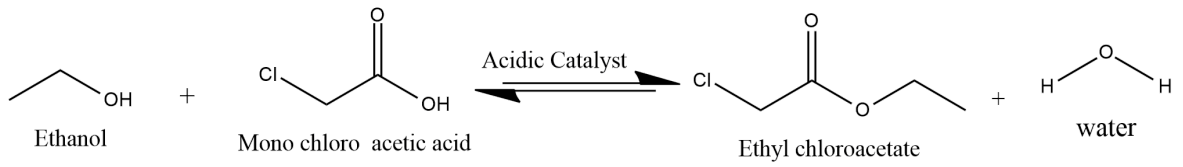

Figure 1: Esterification of Ethanol and Mono chloro acetic acid to form Ethyl chloro acetate

Methodology. To delve into various aspects of getting a synergistically coordinated reaction and separation scheme for RD, understanding of various aspects such as reaction kinetics, vapour liquid equilibrium, and careful catalyst selection are required. The reaction kinetics was studied by varying the reaction conditions, such as temperature, feed molar ratio, stirring speed, and catalyst loading etc., in a batch reactor. The results were fitted to a suitable model equation to obtain the reaction parameters. Theoretical studies for RD were performed using ASPEN plus RADFRAC module. Meticulous selection of RD configuration and distillation policy, such as number of stages, feed location, feed flow rates, reflux ratio and reboiler duty, is required for the desired product yield which is not only complex but possibly have multiple solutions. Initial simulations were performed for twenty stages, out of which four stages were part of the reactive section. All the missing parameters were estimated using the UNIFAC method. As the reactive section comprises Amberlyst-15 catalyst, a temperature constraint of 393 K is set to avoid catalyst deactivation.

Results and discussion. The conversion of MCA achieved is 100%. However, there remains a potential to increase the recovery of ECA as a part of it is carried along to the top with the vapour stream due to the formation of the azeotrope. Another challenge is the removal of water and recovery of ethanol due to its azeotropic mixture with water. A sensitivity analysis with varying feed molar ratios, reflux ratio and catalyst loading could provide better foresight to improve the overall product yield.

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Propane Dehydrogenation to Propene with CO_2 on Zn(Ga)-BEA Zeolites

S. Orlyk[1], A. Kapran[1], Y. Millot[2], S. Dzwigaj[2*]

[1]*L.V. Pisarzhevskii Institute of Physical Chemistry, NAS of Ukraine, Kyiv, Ukraine*
[2]*Laboratoire de Réactivité de Surface, Sorbonne Université-CNRS, Paris, France*
**stanislaw.dzwigaj@sorbonne-universite.fr*

Keywords: propane dehydrogenation with CO_2, Zn(Ga)-BEA zeolites, acid-base characteristics.

Introduction. Oxidative dehydrogenation of alkanes, in particular propane to propene mediated with CO_2 (CO_2-PDH), is considered a promising alternative to the oil-based cracking processes of olefins production [1]. Among the promising catalysts for CO_2-PDH are those based on BEA zeolite with incorporated heteroelements [2]. An effect of acid-base characteristics of Zn(Ga)-BEA zeolites on their catalytic performance in the CO_2-PDH processs is presented in this work.

Experimental/methodology. The catalyst samples, prepared by two-step post-synthesis procedure [3], including full dealumination of BEA specimen followed by introducing Zn^{2+}, Ga^{3+}(Nb^{5+}, Ta^{5+}) cations into T-positions of zeolite framework, were characterized using the XRD, XPS, MAS NMR, low-temperature N_2 ad/desorption, C_3H_8/C_3H_6 (CO_2, NH_3)-TPD, TPO-O_2, and FTIR-Py techniques. Catalytic experiments were carried out in a flow-type quartz reactor at atmospheric pressure, at a temperature of 823–923 K, and a gas hour space velocity (GHSV) of 6000 h^{-1}. The reaction mixture composition for CO_2-PDH was 2.5 vol. % of C_3H_8 and 15 vol. % CO_2 in He.

Results and discussion.

The adjustment of acid–base characteristics of BEA zeolite-based catalysts by preliminary dealumination of the original zeolite (Si/Al = 17) followed by the incorporation of heteroelement cations ensures the formation of MSiBEA compositions (Si/Al = 1000) with significantly reduced overall acidity and basicity.

The content of gallium in the zeolite matrix has a significant effect on the acid–base characteristics of catalysts. Weak and medium-strength Lewis acid sites of Ga(III)-O(H)-Si structure formed by isolated gallium atoms play a key role in the target process over Ga(Ta,Nb)SiBEA catalysts. Propylene yield reaches 37% (873 K) in the presence of $Ga_{4.0}$SiBEA catalyst. At the same time, a higher propylene formation selectivity of 70-77% was achieved over $Ga_{2.0}Ta_{2.0}$SiBEA (Table).

Propylene selectivity of 74% and yield of 22% was achieved over the $Zn_{1.0}$SiBEA catalyst, which is characterized by the presence of mainly medium-strength acid (LAS are Zn^{2+}) and basic (O^{2-} anions and oxygen vacancies) sites on the surface of [Zn–O–Si] structures. An important factor in the selectivity of the $Zn_{1.0}$SiBEA catalyst is the absence of Bronsted acid sites on its surface capable of protonating the formed olefin, intensifying the further side cracking processes with carbonization of the catalyst surface.

Table. CO_2-PDH process parameters over Zn,Ga(Ta,Nb)-BEA catalysts

Catalyst	X_{C3H8}, %	S_{C3H6}, %	Y_{C3H6}, %	TOS, min
$Zn_{1.0}$AlBEA	37–11	23–42.5	9–5	
$Zn_{1.0}$SiBEA	32–27,5	73–76	23–21	
$Ga_{1.0}$SiBEA	28–27	71–74	20	
$Ga_{2.0}$SiBEA	31–27	63–62	19,5–17	20–120 (150)
$Ga_{4.0}$SiBEA	57.5–45	64–73	37–35	
$Ga_{2.0}Ta_{2.0}$SiBEA	29–26	77–76	22–20	
$Ga_{2.0}Nb_{2.0}$SiBEA	20–19	70–71	14–13	

T = 923 K is for Zn-containing catalysts, *T* = 873 K is for Ga-containing catalysts.

Thus, propylene production with acceptable selectivity and yield parameters in the process of propane dehydrogenation with CO_2 over M-BEA zeolite catalysts is achieved at the balancing of their acidic and basic characteristics.

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Preparation of esters of tertiary alcohols

M.Kotova, A. Šnebergerová a T.Vargina

Department of Organic Technology, University of Chemistry and Technology, Prague, Czech Republic
**maria.kotova@vscht.cz*

Keywords: esters of tertiary alcohols, Lewis acids, acetylation

Introduction.

Esters are a large class of organic compounds widely used in many fields of chemical industry. Most esters have a characteristic, pleasant smell and are therefore often used in the fragrance industry [1]. The development of efficient synthetic routes to carboxylic acid esters is still of great interest because fine chemicals often contain ester unit as the functional group [2]. The usual methods involve the condensation reaction between an alcohol and a carboxylic acid in the presence of a mineral acid. This synthetic approach results in good yields with primary alcohols, limited yields with secondary alcohols, and poor yields with tertiary ones. The main goal of the work was to find a simple and efficient way for the direct synthesis of esters of tertiary alcohols and to optimize reaction conditions (catalyst, catalyst amount, solvent). Dimethylbenzylcarbinol and 1adamantanol were chosen as model alcohols.

Experimental/methodology.

Various synthetic procedures such as Fischer esterification, Steglich esterification, and acylation with functional derivates of acetic acid catalyzed by Lewis acids and basic catalysts to obtain esters of tertiary alcohols were tested. The preparation of esters by Fischer and Steglich esterification was performed according to literature procedures [1]. Acylation of alcohols with functional derivates of acetic acid catalyzed by Lewis acids and basic catalysts was performed the following way: to a mixture of tertiary alcohol (1 mmol), dichloromethane (10 ml), and catalyst (0.1 mmol) acetic anhydride or acetyl chloride (10 mmol) was added. The mixture was stirred at room temperature for 1-6 h. Samples were taken at different intervals during the reaction to determine conversion and selectivity. The samples were neutralized with a 5% solution of sodium bicarbonate and analyzed using GC (DB-5, non-polar column, FID) or GS/MS (column: DB-5-ms, length: 35 m, diameter: 0.20 nm, thickness: 0.33 μm) in order to identify the products.

Results and discussion.

It was found that in reactions under conditions of Steglich and Fischer esterification good results were not achieved. In the case of Fischer esterification of acetic acid with dimethylbenzylcarbinol only the undesired product of dehydration 2-methyl-1-phenylprop-2-ene was obtained. Fischer esterification of acetic acid with 1-adamantanol didn't take place. Although under conditions of Steglich esterification, the desired product was formed, the conversion of alcohols in both cases was only 52-56 % after 24 hours. Acylation with functional derivates of acetic acid catalyzed by basic catalysts (4-dimethylaminopyridine, triethylamine, pyridine) had given good results (total conversion, selectivity up to 95 %), and no side products were detected in the reaction mixture. Acylation with acetic anhydride catalyzed by hard Lewis acids ($AlCl_3$, $FeCl_3$, $ZnCl_2$) took place with high selectivity (over 99 %) to the desired ester. On the other hand, acylation under the same conditions with acetyl chloride tended to either undesired dehydration of dimethylbenzylcarbinol to give alkene or nucleophilic substitution of hydroxyl group in 1-adamantanol leading to the formation of 1-chloradamantane. According to the obtained results, we can conclude that Lewis acids and 4-dimethylaminopyridine are useful catalysts for the acetylation of tertiary alcohol by acetic anhydride.

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Iridium nanoparticles deposited onto nanotubes supports for the hydrogenation of nitrobenzene: Effect of the support nature

Edgardo Leal-Villarroel[1], Cecilia C. Torres[2], Phillipe Serp[3] and C. H. Campos[1].

[1]*Universidad de Concepcion, Concepcion, Chile*
[2]*Universidad de Andres Bello, Talcahuano, Chile*
[3]*Université de Toulouse, UPR 8241 CNRS, Toulouse, France*
edleal@udec.cl

Keywords: Hydrogenation, Nitrobenzene and Nanotubes

Introduction.
The selectivity production of primary amines is a global target, and this market represents a mundial production of four million tons per year [1]. The hydrogenation of nitrobenzene (NB) to obtain aniline (AN) is one of the model reactions to evaluate the efficiency and operational stability of new catalysts formulation. In this field, the nanomaterials-based heterogeneous catalysts arise as a hot-topic due to structural properties conferred by quantum effects. Among them, the noble metals supported onto nanotubes provide a unique environment to produce highly active and stable catalysts mainly by the confinement effects onto their inner surface. This research proposes a comparison between two different kinds of supports: carbon nanotubes (CNT) and TiO_2 nanotubes (TNT) to prepare Iridium (Ir) supported catalyst for the heterogeneous hydrogenation of NB to produce AN.

Experimental/methodology.
Nanotube supports were prepared according to our previous reports [2, 3]. Different metal loadings (0.25, 0.5, 1.0 and 2.0 wt %) were prepared using $Ir(acac)_3$ as metal precursor. The obtained solids were calcined at 623K and reduced using H_2 at 573K. The catalysts were labelled as xIr/CNT or xIr/TNT, respectively, where x correspond to Ir loading. The physicochemical properties of the catalyst were analyzed by XRD, N_2 adsorption-desorption isotherms, H_2-TPR, H_2-chemosoprtion, TEM and XPS characterization techniques. The catalytic activity was measured in a batch stainless steel batch reactor with 50 mg of catalyst, a molar ratio NB/Ir of 250 in ethanol as solvent at 303 K, 10 bar of H_2 pressure and constant stirring to avoid diffusional control. The periodic samples of the reaction were analysed in a GC with FID detector.

Results and discussion.
The physicochemical characterization of the Ir supported catalyst displayed that the nanotubes surface area remains constant after the metal deposition. In addition, the H_2-chemosorption showed a decrease of the metal dispersion with the increase of metal loading. The presence $Ir^{\delta+}$ surface species – detected by XPS – increased with the increase of the metal loading particularly in the xIr/TNT catalysts. The catalytic performance showed that all the NB conversion profiles fitted a pseudo-first kinetic model and high selectivity to the desired product was found. Intermediary products such as nitrosobenzene, N-phenyl-hydroxylamine or other condensation products were not detected. Among the different catalytic systems xIr/CNT catalysts series displayed a higher efficiency in comparison with the xIr/TNT catalysts. Furthermore, the best catalytic efficiency was shown by the 1.0Ir/CNT catalysts reaching 5 continuous catalytic cycles remaining the maximum of conversion and selectivity to AN production.

Acknowledgments
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Poster: Utilisation of iron carbonyls in Pd-catalysed carbonylation in batch and flow mode

P. Lopatka, M. Markovič, P. Kóóš, M. Králik, T. Gracza

Institute of Organic Chemistry, Catalysis and Petrochemistry, Slovak University of Technology, Bratislava, Slovak Republic
pavol.lopatka@stuba.sk

Keywords: flow chemistry, homogeneous carbonylation, iron (II) tetracarbonyl bromide

Introduction.

The carbonylation transformation has not yet gained widespread adoption in research and industry. The main reason is the reluctance of scientists to work with the highly poisonous gas - carbon monoxide. Utilisation of CO surrogates can reduce safety risks, but such approach relies on the compatibility between the conditions for gas generation and its consumption, which can complicate post-reaction processing. Iron pentacarbonyl has been successfully applied as an *in situ* CO donor in the oxycarbonylation of unsaturated alcohols [1,2]. However, its further application in the carbonylation transformation of aryl bromides has proven difficult due to the problematic isolation of products [3]. The use of iron (II) carbonyl halide compounds can avoid such problems.

Experimental/methodology.

Herein, we apply iron (II) tetracarbonyl bromide [4] as an *in situ* CO surrogate in the continuous Pd-catalyzed carbonylation of aryl bromides (Fig. 1). Pd-catalyzed carbonylations were performed within a 40-minute residence time using a stainless steel coil reactor. The NMR, HPLC-MS, and GC-FID techniques were used for the analysis of conversions and yields of products.

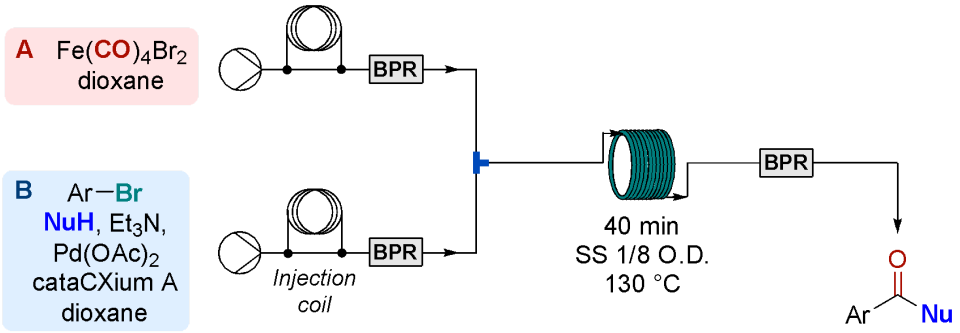

Figure 1. Experimental setup for the continuous carbonylation of aryl bromides.

Results and discussion.

The initial experiments performed on 4-bromoanisole in screw cap vials yielded high amounts of the desired amide, as determined by GC-FID. Further optimization of the parameters for the flow system, such as temperature, pressure, catalyst and ligand loading, and residence time, resulted in process-intensified reaction conditions for the Pd-catalyzed Heck-type carbonylation. Iron(II) tetracarbonyl bromide was successfully used as the CO donor in nearly stoichiometric amounts. A variety of carboxylic acid derivatives were also prepared on a multigram scale by a direct pumping of stock solutions using the HPLC pumps. Additionally, our procedure was applied in the synthesis of moclobemide, a drug used to treat depression and social anxiety.

Acknowledgments

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Impact of O-defects and Ru species on aerobic oxidation of benzyl alcohol on high-surface-area Ru/TiO_2 catalysts

Van Hung Mac[1,2], Katja Neubauer[1], Ali M. Abdel-Mageed[1*]

[1]*Leibniz-Institut für Katalyse e. V., Albert-Einstein-Str. 29a, 18059 Rostock, Germany*
[2]*Hanoi University of Science and Technology, 100000 Ha Noi, Viet Nam*
[*]Ali.abdelmageed@catalysis.de

Introduction. The selective oxidation of alcohols is a major step for the production of wide range of chemicals, in particular the solvent-free selective oxidation of benzyl alcohol using oxygen.[1] Ru has attracted considerable interest in catalysis not only because of its relatively low cost compared to commonly studied and industrially applied noble metals such as Au, Pt, Pd, but also due to its tunability by different support effects, especially in combination with TiO_2.[2] In this work, we focused on the systematic study and optimization of supported catalyst on high specific-surface-area (SSA) TiO_2 supports for the liquid-phase aerobic oxidation of benzyl alcohol at ambient pressure. Here, we aim at the identification of structure-reactivity descriptors for controlling the activity and selectivity by screening different structural features, focusing in the beginning on the impact of O-vacancy defects and the nature of the Ru species.

Experimental. Ru/TiO_2 catalysts with a similar amount of Ru were prepared by impregnating TiO_2 supports doped with varying amounts of SiO_2 (supplied by Venator) using $RuCl_3.xH_2O$ salt.[3] Prior to measurement and characterization, the catalyst was pretreated at 200 °C under a flow of H_2. The catalytic measurements were carried out in a three-neck round bottom flask with 10 ml of benzyl alcohol under magnetic stirring without further addition of a solvent. Reaction mixtures are analyzed with GC-MS and confirmed using ^1H and ^{13}C NMR. Catalysts were studies before / after reaction with different characterizations

Results and discussion. Catalytic measurements are done after reductive treatment which results in the formation of highly dispersed Ru nanoclusters and measurable fraction of isolated Ru^{3+} ions (see previous results in Ref.[3]). The catalytic activity of Ru/TiO_2 catalysts for the selective aerobic oxidation of benzyl alcohol depends significantly on the level of SiO_2 doping. Based on previous studies on similar catalysts, the increase of SiO_2 leads to the decrease of the concentration of O-defects.[4] By plotting the conversion of benzyl alcohol versus the amount of SiO_2 in the catalyst we see an inverted volcano type dependence of rate of conversion on the amount of SiO_2 (Figure 1), and thus on the concentration of O-defects, with the highest conversion for SiO_2-free Ru/TiO_2 catalyst (highest O-defect concentration). Selectivity for benzaldehyde, in contrast, reaches highest value at a doping level of 4% SiO_2, which was previously correlated with moderate support reduction (O-defects concentration). We observed another major product confirmed, by 1H NMR measurements, as dibenzyl ether. The quantity of this product is similar to benzaldehyde but follows a trend similar to the changes in benzyl alcohol conversion (directly proportional to conversion). Interestingly the selectivity toward dibenzyl ether was increasing with the decrease of reaction temperature in the range between 150 and 80 °C while at the same time selectivity to benzaldehyde goes in the opposite direction. Origin of the activity and selectivity on these catalysts shall be discussed in the light of additional results on Ru/TiO_2 catalysts based dominantly on loading Ru in an atomically dispersed form and based on detailed structural characterization with different spectroscopic and microscopic tools.

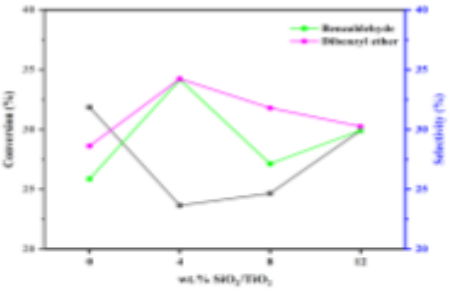

Figure 1. Benzyl alcohol conversion and product selectivity on Ru/TiO_2 with different SiO_2 doping at 150 °C

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Prins cyclisation of isoprenol and isovaleraldehyde over micro- and mesoporous catalysts for production of Florol®

P. Mäki-Arvela[1*], B. Lasne[1], Z. Vajglová[1], N. Kumar[1], A. Aho[1], M. Peurla[2], J. Sánchez-Velandia[3], C. Mondelli[4], J.Pérez-Ramirez[4], D. Yu. Murzin[1]

[1] *Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi University, 20500 Turku/Åbo, Finland*

[2]*Faculty of Medinice, University of Turku, 20500 Turku/Åbo, Finland*

[3]*Grupo de Investigación Fitoquimica Universidad Javeriana, Pontificia Universidad Javeriana, Bogotá, Colombia*

[4]*Institute of Chemical and Bioengineering, department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1, 8093 Zürich, Switzerland*

[*]*pmakiarv@abo.fi*

Keywords: Florol, Prins cyclization, zeolite, mesoporous material

Introduction. Prins cyclisation of isoprenol with isovalerladehyde for production of tetrahydropyranol (THP), known as a commercial fragrancy product Florol®, was investigated over acidic heterogeneous micro-and mesoporous catalysts (Fig. 1a) with the special interest on revealing the effect of the textural properties on catalyst performance. In addition, to support the experimental observations, also DFT calculations were performed to unravel the possible reaction mechanism.

Experimental/methodology. Several heterogeneous catalysts including H-Beta zeolites with varying SiO_2/Al_2O_3 ratio, microporous H-USY-30 and its alkali treated counterpart as well as micro-mesoporous Beta zeolite-MCM-41 hybride materials and iron modified Beta zeolite were tested. The catalyst were charaterized by several methods, such as nitrogen adsorption, acidity by pyridine adsorption-desorption FTIR, SEM and TEM. Prins cyclisation of isovaleraldehyde (IVA) with isoprenol (IP) was investigated in a glas reactor using dimethylcarbonate as a solvent. In a typical experiment 10 mmol of IP and 50 mmol of IVA were used together with 0.15 g catalyst and a high stirring speed and small catalyst particles were used to suppress mass transfer limitations. DFT calculations with Perdew-Burke-Ernzerhoff method were performed.

Results and discussion. The results demonstrated that mildly acidic H-Beta-300 afforded the highest selectivity to THP (72%), while more acidic zeolite catalysts exhibited more prominent deactivation and lower selectivity to THP. Dehydration of THP also occurred in some extent forming dihydropyrans (DHP).

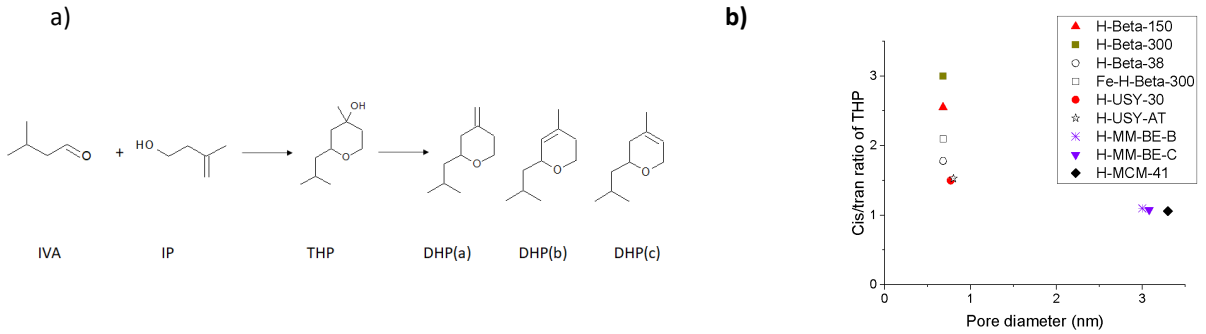

Fig. 1. a) A simplified reaction scheme for Prins cyclisation of isoprenol (IP) with isovaleraldehyde (IVA) for production of tetrahydropyranol (THP) and its dehydrated counterparts, dihydropyrans (DHP), b) cis/trans ratio of THP isomers as a function of the catalyst pore size.

The most interesting result was the effect of the pore size on the cis/trans ratio of THP (Fig. 1b), namely a high cis/trans pyranol ratio was obtained over microporous zeolites, while opposite results were seen for mesoporous materials produced lower cis/trans pyranol ratio. In the final work the effect of reaction conditions, such as temperature and reactant ratio will be discussed. Furthermore, a special emphasis will

be put on correlation of catalyst properties with their performance. Finally a plausible reaction mechanism proposed based on DFT calculations will be discussed.

Layered Double Hydroxides as catalysts for Baeyer-Villiger oxidation

O. Gorlova[1], I. Paterová[1*], J. Kocík[2], K. Peroutková[2], Z. Tišler[2]

[1]*Department of Organic Technology, ICT Prague, Technická 5, 166 28 Prague 6, Czech Republic*
[2]*ORLEN UniCRE a.s., Revoluční 1521/84, 400 01 Ústí nad Labem, Czech Republic*
[*]*Corresponding author: iva.paterova@vscht.cz.*

Keywords: hydrotalcite, hydrogen peroxide, Baeyer-Villiger oxidation, LDH, myrtenal, β-cyclocitral

Introduction.

Baeyer–Villiger (BV) oxidation is one of the most important tools for the synthesis of esters from ketones or aldehydes using peroxides or peroxyacids as oxidizing agents [1, 2]. It should also be underlined that the ester may not be the main desired product. Under suitable reaction conditions, subsequent hydrolysis of the resulting ester to a more valuable ketone or aldehyde can be performed [3]. It is known from the literature that catalysts modified with e.g. tin [3] or iron [4] are very active for BV oxidation. One of several types of catalysts that can be used for this reaction are double layered hydroxides (LDH), or hydrotalcite-like compounds [5]. The course of BV oxidation also depends on the structure of the starting substance [1-5]. To compare this effect, 2 substances with different structures were chosen, namely myrtenal as a representative of bicyclic compounds and β-cyclocitral as a representative of monocyclic substances. BV oxidation was carried out in the presence of hydrogen peroxide as an oxidizing agent and LDH with different contents of tin and iron as catalysts.

Experimental/methodology.

LDH with different molar ratios of Sn/Fe/Mg/Al (Sn/Zn/Mg/Al) ions were synthesized by co-precipitation method at constant pH value (pH = 9.5) and constant temperature (T = 60 °C). The solution of metal precursors was precipitated with a basic solution of potassium hydroxide and carbonate. The precipitated solid was filtered off, washed, dried overnight and subsequently transformed by calcination in air at 400 °C for 5 h to mixed oxides. The Baeyer-Villiger oxidation was carried out in a 25 ml magnetically stirred round bottom flask equipped with a reflux condenser, containing a mixture of 0.1 g of catalyst, 0.5 g of starting material, 3 g of solvent and tempered to the desired temperature. Hydrogen peroxide (3.2 eq.) was gradually dosed to the mixture at 10-minute intervals in 12 doses.

Results and discussion.

All prepared materials were characterized by different analytical methods. Mixed oxides were tested as catalysts for Baeyer-Villiger oxidation of myrtenal and β-cyclocitral and for subsequent hydrolysis of the resulting formates to the desired products. The effect of the type and amount of incorporated metal (Sn, Fe), and the starting substance structure was evaluated. The activity of MgAl, ZnAl and ZnMgAl mixed oxides was compared. Mixed oxides based on ZnAl hydrotalcites, both tin-modified and unmodified, appeared to be the most active ones. After 5 h of reaction, almost 100% conversion of myrtenal and 95% selectivity to nopinone was achieved. Mixed oxides containing iron in the structure were not as active as those ones containing tin. The maximum myrtenal conversion achieved did not exceed 40 %. The selectivity to nopinone was also quite low - only 30 %.

Acknowledgments

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Isolated Copper Sites on Graphite Nanoplatelets for Ullman-type C-O Coupling

Vincenzo Ruta,[1] Dr. Mark A. Bajada,[1] and Prof. Dr. Gianvito Vilé*,[1]

[1]*Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano (Italy)*
[*]*Corresponding author email: gianvito.vile@polimi.it*

Introduction. For the past 20 years, cross-coupling reactions have been crucial in organic and pharmaceutical synthesis, as they allow for the formation of C-C, C-O, and C-N bonds in a single step [1]. Among the most widely used reactions, Ullmann condensations play a significant role in the formation of C-O bonds, enabling the synthesis of variously substituted diaryl ethers using inexpensive copper catalysts. However, the reaction also has its drawbacks, including harsh reaction conditions, the need for bulky and expensive ligands, and the low efficiency of existing protocols [2].
We introduce herein a novel single-atom Cu catalyst supported on tetraethylenepentaminopyrrole-functionalized graphite nanoplatelets (Cu_1/TEPAP-GNPs) that has been synthesized in a controlled manner, thoroughly characterized, and demonstrated in Ullmann-type condensation reactions.

Experimental/methodology. Catalyst preparation was performed in a two synthesis approach, via graphite nanoplateletes synthesis and metal immobilization. A battery of structural and spectroscopic analysis (ICP, XRD, XPS, XAS, TEM, FTIR, NMR) was applied to elucidate the main catalysts properties. For the catalytic tests, the phenol (0.5 mmol) and aryl bromide (0.75 mmol) were dissolved in a glass tube in 2 mL of solvent, and the catalyst (8 mg) was added. The tube was sealed and heated at the specific temperature, ranging from 90 to 150 °C. The reaction mixture was analyzed via high pressure liquid chromatography, determining conversion, selectivity, and product yield. DFT calculations (VASP code) were applied to determine the reaction mechanism.

Results and discussion. We began our work by conducting the copper-promoted coupling of phenol and bromobenzene, optimizing the process in terms of catalyst amount, solvent, and reaction. By correlating these results with the catalyst structural properties, we found out that the presence of the polyaminic linker on the catalyst surface allowed improved activity and selectivity (reaction rate = 201 $mmol_{prod}mol_{Cu}^{-1}h^{-1}$, product selectivity >90%), while its absence was detrimental to the process (reaction rate = 20 $mmol_{prod}mol_{Cu}^{-1}h^{-1}$). This pointed to the role of the polyaminic linker as a ligand, stabilizing and activating the isolated metal center. The flexibility of our protocol was confirmed by testing variously decorated phenols and aryl bromides, showing the excellent catalytic performances of our materials. Moreover, time-on-stream studied confirmed the stability of this materials over 24 h of operation. DFT calculations were finally applied to postulate a reaction mechanism on the Cu isolated sites, showing that the interaction between the catalyst and reactants is thermodynamically favorable and provides a reasonable explanation for the observed kinetics.

Figure 1. *HRTEM of the catalysts (a), schematic representation of the Ullmann coupling reaction on the heterogeneous catalyst (b), XPS spectra of C 1s (c), N 1s (d), Cu 2p (e) of the catalyst; and XANES spectra (f).*

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Simulation based design of Simulated Moving Bed Reactor for the production of 2-phenyl Ethyl Acetate

Kapil Satya Pal Singh*, Sanjay M. Mahajani

Department of Chemical Engineering, IIT Powai, Mumbai-400076
Corresponding Author: Kapil Satya Pal Singh (kapiljayantt@gmail.com)

Keywords: Simulated-moving bed reactor, Triangle theory, Pareto plot

Introduction. Simulated moving bed reactor (SMBR) is a single-unit operation that have four sections and each section have specific number of beds. In this, adsorption and desorption occur concurrently with the reaction and separation. That makes it a viable option for equilibrium limited reactions, to achive complete conversion of limiting reactant. It has a total thirteen number of degrees of freedom i.e., feed and desorbent concentrations, and their flow rates, raffinate and extract flow rates, four sectional flow rates, switch time and column dimensions which makes its dsign a challanging task. The complete process of SMBR is followed by desorption recovery from both raffinate and extract phases, which mainly governs the operating cost. On the other hand, the capital cost depends on productivity.[1-2] Therefore, the objective of this study is to get minimum solvent requirement and maximum productivity using a simplified approach. Instead of mathematical optimization clubbed with simulation which is computaionally exhaustive. For design optimisation, the reaction of interest undertaken is 2-phenyl ethyl acetate synthesis by reacting 2-phenyl ethyl alcohol with acetic acid, in the presence of catalyst/adsorbent Amberlyst-15.

Methodology. The solution methodology aodpted is based on Triangle theory which is well developed for simulated moving bed (SMB) without reaction.[2] It uses linear adsorption isotherm and puts constaints on flow rate ratios (namely as m_1, m_2, m_3 and m_4) to ensures complete conversion of limiting reaction, raffinate, and extract purity. This theory is further extended to SMBR (SMB with reaction). The SMBR model equation was solved in MATLAB with suitable boundary conditions. To begin with the design optimization, column area, feed and desorbent concentration, feed flow rate and SMBR configuration were assumed.

Results and discussion. Initially, the mass flow rate ratios m_1 and m_4 were assigned a high value (as per constraints) so that extract purity is satisfied.It was reduced slowly to come up with the best design. Although, m_2 and m_3 had a range of values as per constraints. The feasibility of m_2 -m_3 pairs were studied and they were plotted on triangle digram,as shown in Figure 1(a). Further, the effect of various

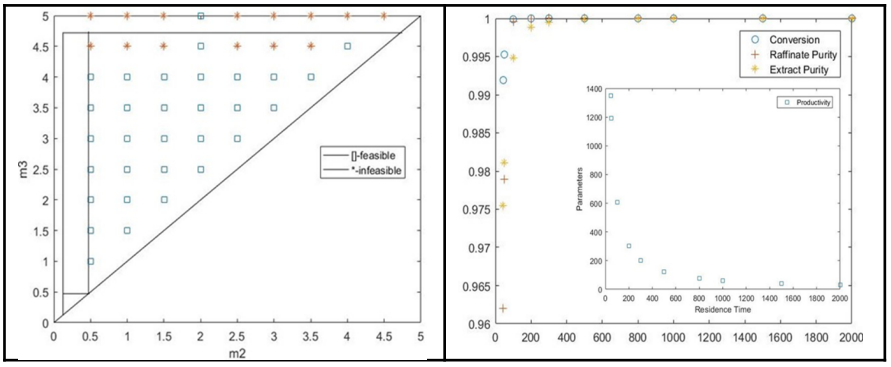

Figure 1. (a) Triangle theory diagram (b) Effect of residence time

parameters were studied such as effect of residence time (as shown in 1(b)), flow rates of all four sections, pseudo solid velocity etc. The parameters were optimized for m_2-m_3 feasible pairs through diferent paths that gave minimum desorbent and maximum productivity. Productivity vs desorbent values were plotted to arrive at a plot similar to Pareto plot which shows maxium productivity and corrosponding mimimum value of desorbent required.

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MoO_3-MCM materials as effective catalysts in Prins reaction of isoprenol with butanal

E. Vrbková[1], L. Dolejšová Sekerová[1], E. Vyskočilová[1*]

[1]*Dpt. of organic technology, University of Chemistry and Technology Prague, Prague, Czech Republic*
[*]*eliska.vyskocilova@vscht.cz*

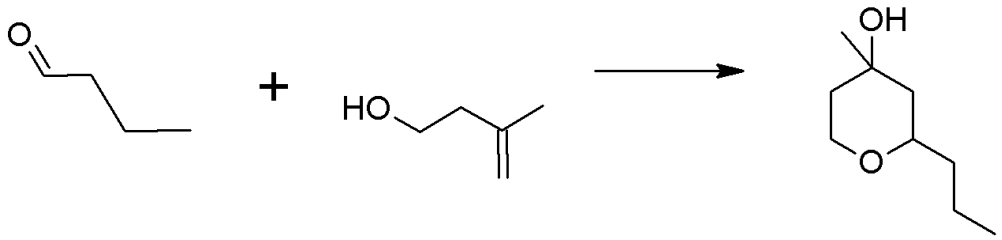
Keywords: Prins reaction, 4-methyl-2-propyltetrahydro-2*H*-pyran-4-ol, MCM-41

Introduction. Prins reaction of isoprenol with butanal provides important an intermediate (4-methyl-2-propyltetrahydro-2*H*-pyran-4-ol), which can be acylation to 4-methyl-2-propyltetrahydro-2*H*-pyran-4-yl acetate desired fragrance with fruity and rose scent known, e.g., as Clarycet®[1]. Lewis acids are suitable catalysts for this reaction [2,3].

Experimental/methodology. Materials were prepared by wet impregnation method using commercially available MCM-41 and water solution of ammonium molybdate. Catalytic testing was performed in batch arrangement, and samples of the reaction mixture were analyzed using gas chromatography (FID, non-polar column).

Results and discussion. Within this work, we prepared MCM-41 modified with different MoO_3 amounts. These materials were thoroughly characterized (nitrogen physisorption, acidity – temperature programmed desorption, elemental composition, etc.). The activity of prepared materials was tested in the Prins reaction of isoprenol with butanal. The influence of various reaction conditions (catalyst type, solvent, water addition) was tested. It was shown that modification of MCM-41 with MoO_3 led to a significant increase of catalytic activity (butanal conversion at 4 hours of reaction: 7% for MCM-41 compared to 93% for material 5wt.% of MoO_3-MCM-41). Water addition to the reaction mixture positively influenced the selectivity to desired substituted tetrahydropyranol (4-methyl-2-propyltetrahydro-2*H*-pyran-4-ol). The next step will be the production of the product in a higher amount followed by acylation.

Figure 1. Reaction scheme – Prins reaction of isoprenol with butanal providing 4-methyl-2-propyltetrahydro-2*H*-pyran-4-ol



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Deoxygenative Silylation of C(sp^3)–O Bonds with Hydrosilane by Supported-Gold Nanoparticles catalyst

Y. Yasui[1], M. Doi[1], H. Miura[1,2,3*], T, Shishido[1,2,3]

[1] *Tokyo Metropolitan University, Tokyo , Japan*
[2] *Research Center for Hydrogen Energy-based Society, Tokyo , Japan*
[3] *Elements Strategy Initiative for Catalysts & Batteries Kyoto University, Kyoto , Japan*
[*] *miura-hiroki@tmu.ac.jp*

Keywords: C(sp^3)–O activation, Gold catalyst, Silylation, Hydrosilane

Introduction.

Deoxygenative transformation of C–O bonds attracts much attention since reducing the oxygen content of biomass-derived molecules is important from the viewpoint of carbon resource circulation. Deoxygenative silylation of C–O bond are an ideal method for synthesizing organosilicon compounds which are widely used as chemical intermediates in organic synthesis and resources of silicon polymers. Hydrosilanes are a promising source of silyl moiety owing to their high stability, low price, and commercial availability. Nevertheless, cross-coupling between carbon electrophiles with hydrosilanes to give organosilicon compounds is still rare due to high nucleophilicity of hydride of hydrosilane, consequently resulting the formation of reduced hydrocarbons.

Herein, we describe that supported Au catalysts showed high activity toward deoxygenative silylation of inactive C(sp^3)–O bond in alkyl acetate to give alkylsilanes.

Experimental/methodology.

Supported Au catalysts were prepared by precipitation method using $HAuCl_4$ as a precursor. Au was deposited on the support by adding a metal oxide and urea as a pH adjuster to an aqueous $HAuCl_4$ solution. The resulting powder was calcined in air and reduced in at 200 °C for 1 h to obtain the supported Au catalyst.

Results and discussion.

The deoxygenative silylation of decyl acetate (**1a**) with triethylsilane (**2a**) was carried out in the presence of TiO_2 supported Au catalysts. The corresponding alkylsilane (**3a**) was obtained in 92% yield. The reaction did not proceed by using supported Ni, Cu, Pd, Ag and Pt catalysts. Furthermore, the supports for Au nanoparticles were important for highly selective C–Si bond formation, and surface Lewis acidic property of supported catalysts was essential for the activation of alkyl electrophiles. Various alkyl esters and propargyl carbonates participated in the Au-catalyzed deoxygenative silylation with hydrosilanes to give the corresponding alkylsilanes and allenylsilanes. (Figure 1) Detailed mechanistic investigation revealed that generation of silyl radical via the single-electron transfer from hydrosilane to Au nanoparticles is responsible for unusual reactivity of hydrosilanes.

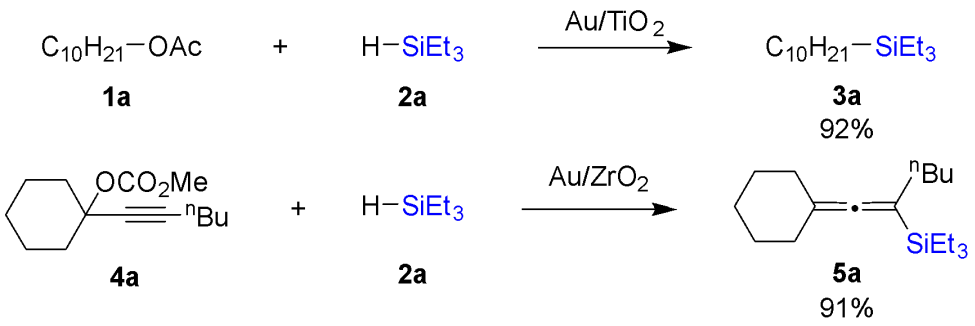

Figure1 Deoxygenative silylation of C(sp^3)–O bonds with hydrosilane

Gas to liquids conversion

Activation of small molecules over binuclear centres embedded in various zeolite topologies

E. Tabor, S. Sklenak[1], K. Mlekodaj[1], A. Kornas[1], D.K. Wierzbicki[2], M. Lemishka[1], R. Pilar, J.E. Olszowka, J. Dedecek[1,*]

[1]*J. Heyrovský Institute of Physical Chemistry of the CAS v. v. i. Prague, Czech Republic*

[2]*Paul Scherrer Institut, Forschungsstrasse 111, 5232 Villigen PSI, Switzerland*

[*]*E-mail: jiri.dedecek@jh-inst.cas.*

Keywords: alpha oxygen, binuclear iron centers, O_2 activation.

Introduction. According to the theoretical prediction, binuclear iron sites in various zeolitic matrices are expected to split O_2 with a formation of α-O.[1] The unique property of α-O lies in the ability to oxidize highly stable molecules (methane) already at ambient temperature.[2] Direct application of O_2 for transforming hydrocarbons into value-added oxygenates, being a platform for chemicals and energy vectors, is of paramount importance for sustainable catalysis. Yet, the formation of fully functioned iron sites (capable of splitting O_2 and oxidizing methane with α-O) was confirmed experimentally for FER and very recently also for Al-rich *BEA zeolites. The occurrence of these active sites requires a high population of Al pairs (Al-O-Si-O-Al sequences in one zeolitic ring) which can stabilize divalent cations and their proper geometrical arrangement in two axial rings in the vicinity of ~7 Å.[1,2].Both of those conditions are met in the FER and *BEA topologies. However structural differences local geometry of divalent cation, distance between iron sites, and Al atoms organization) of FER and *BEA matrix may affect the final performance of binuclear Fe(II) sites in splitting O_2 and subsequent oxidation reactions. These differences were confirmed in the value of calculated energy barrier of O_2 activation, which is form Fe-*BEA varies (31.4 kcal/mol) significnaly higher that for Fe-FER(24.9 kcal/mol).[1] This work compares the redox behavior of binuclear Fe(II) sites in *BEA and FER topologies during O_2 activation studied by in-situ XAS and Mössbauer spectroscopies and subsequent interaction with methane as a testing reaction.

Experimental/methodology. Two zeolites of FER (Si/Al 8.5) and *BEA (Si/Al 5) topology with hight population of Al pairs were studied in their Fe-forms (Fe/Al ~0.05, impregnation from the organic solution of $FeCl_3$) by in-situ by Mössbauer and X-ray adsorption spectroscopy and activity tests with FTIR and mass spectrometry detection of the reaction products.

Results and discussion. Mössbauer and XAS spectral characteristics of evacuated Fe-FER and Fe-*BEA confirmed the presence of atomically dispersed Fe(II) cations, however the local geometry of iron sites in the plane of the rings is slightly different – square-planar in the case of Fe-FER and rather square-pyramidal for Fe-*BEA, which is in agreement with the DFT results. Interaction of both samples with O_2 reveals significant differences in samples behavior, indicating formation of a new band at Mössbauer spectra with parameters typical for α-O. In the case of Fe-FER not only the oxidation state but also the geometry of the iron sites is strongly affected by the interaction with O_2, which is reflected on XAS spectra. In-situ XAS spectra registered after the interaction of α-O formed over Fe-FER and Fe-*BEA with methane confirmed that the redox cycle occurred and Fe active sites were restored. Activity tests with mass spectrometry detection revealed the presence of oxidation products, methanol and CO_2 (attributed to signals m/z 31 and 44 respectively), directly in the gas stream. Both samples were stable in three consecutive redox cycles. The presented study proved the differences in the behavior of binuclear iron sites formed in FER and *BEA topologies in both steps of the redox cycle, the activation of O_2, and the employment of formed α-O in the oxidation reaction. Manifested discrepancies in the activity of binuclear iron sites in FER and *BEA are in line with a slightly higher energy barrier of the O_2 splitting over Fe-*BEA.

Acknowledgments

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Nonoxidative Dehydrogenation of Methanol to Dimethoxymethane over Cu/Hβ-zeolite Bifunctional Catalysts with Tailored Acidic Sites

Chalachew Mebrahtu[1]*, Ruiyan Sun[1], Christian H. Gierlich[1], Regina Palkovits[1]*
[1]*RWTH Aachen University, Aachen, Germany*
*asmelash@itmc.rwth-aachen.de, palkovits@itmc.rwth-aachen.de

Introduction. Transportation is one of the main sectors contributing to global greenhouse gas emissions. Therefore, considerable effort is still required for sustainable mobility. Recently, various CO_2-based compounds such as oxymethylene ethers (OME) have been suggested as potential diesel fuel additives, owing to their excellent ability in reducing soot formation and good compatibility with diesel engines [1]. Among the OMEs, dimethoxymethane (DMM) is the simplest compound and its current production relies on an oxidative reaction route with the formation of H_2O leading to low H_2 efficiency. Therefore, recently, our group presented a novel gas-phase DMM synthesis strategy via the nonoxidative methanol (MeOH) dehydrogenation with the formation of H_2 instead of H_2O [2]. This approach appears to be highly attractive due to the potential closed H_2 circulation, thus improving the overall energy efficiency of the process. However, for selective DMM synthesis via nonoxidative dehydrogenation of methanol, a suitable bifunctional catalyst with both acidic and dehydrogenation sites is necessary.

Experimental/methodology. Herein, Cu/Hβ-zeolite with different acidic sites is employed as a bifunctional catalyst for selective DMM synthesis via nonoxidative dehydrogenation of MeOH. The acidic sites of Hβ-zeolite (Si:Al = 25) were first tailored via dealumination using 2, 4, 8, and 12 M HNO_3 (at 80°C). After the dealumination, 1 wt.% of Cu was introduced using incipient wetness impregnation [3]. Finally, the effect of acidic sites on DMM formation was investigated using a gas-phase fixed bed reactor and the prepared catalysts were rigorously characterized to understand structure-activity relationships.

Results and discussion. Among the prepared catalysts, the sample dealuminated with 8 M HNO_3 (1%Cu/Hβ-DeAl8) presented highest activity and selectivity towards DMM (Fig. 1a). 81.5% DMM selectivity was achieved with a MeOH conversion of 3.7% at 1 atm and 200°C. Removal of Brønsted acidic sites (Fig. 1b) via dealumination allowed to suppress dimethyl ether (DME) formation. Interestingly, an induction period featuring a remarkable rise in DMM selectivity from 41 to 81.5% with time on stream occurred [3]. Detailed characterization results indicate adaptation of Cu species and Lewis acidic sites under reaction conditions resulting in the decisively weaker dehydrogenation and condensation ability for high DMM selectivity.

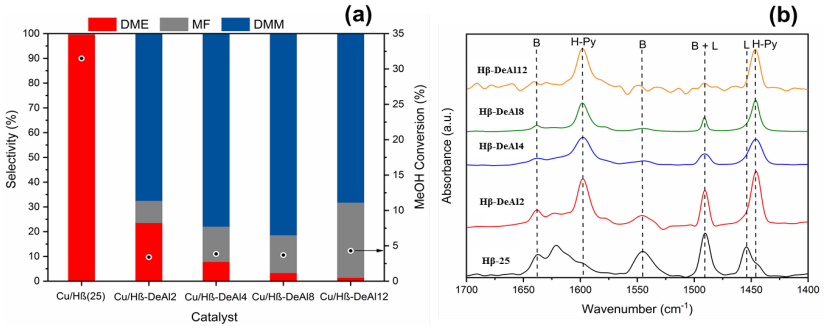

Figure 1. (a) Catalyst screening for the nonoxidative dehydrogenation of MeOH to DMM over 1%Cu/Hβ. Reaction conditions: 1 atm, GHSV = 14549 mL/h/g_{cat}, 0.1 g catalyst: 0.9 g SiC, n(CH_3OH)/n(N_2) = 0.24 (V/V) at 200°C and 1500 min TOS and (b) Py-FTIR spectra of the parent and dealuminated Hβ zeolites.

Acknowledgments

We acknowledge funding by the German Federal Ministry of Education and Research within the project NAMOSYN: Nachhaltige Mobilität durch synthetische Kraftstoffe and by German Research Foundation (PA 1689/22-1).

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Nonoxidative Dehydrogenation of Methanol to Dimethoxymethane over Cu/Hβ-zeolite Bifunctional Catalysts with Tailored Acidic Sites

Chalachew Mebrahtu[1]*, Ruiyan Sun[1], Christian H. Gierlich[1], Regina Palkovits[1]*
[1]*RWTH Aachen University, Aachen, Germany*
*asmelash@itmc.rwth-aachen.de, palkovits@itmc.rwth-aachen.de

Introduction. Transportation is one of the main sectors contributing to global greenhouse gas emissions. Therefore, considerable effort is still required for sustainable mobility. Recently, various CO_2-based compounds such as oxymethylene ethers (OME) have been suggested as potential diesel fuel additives, owing to their excellent ability in reducing soot formation and good compatibility with diesel engines [1]. Among the OMEs, dimethoxymethane (DMM) is the simplest compound and its current production relies on an oxidative reaction route with the formation of H_2O leading to low H_2 efficiency. Therefore, recently, our group presented a novel gas-phase DMM synthesis strategy via the nonoxidative methanol (MeOH) dehydrogenation with the formation of H_2 instead of H_2O [2]. This approach appears to be highly attractive due to the potential closed H_2 circulation, thus improving the overall energy efficiency of the process. However, for selective DMM synthesis via nonoxidative dehydrogenation of methanol, a suitable bifunctional catalyst with both acidic and dehydrogenation sites is necessary.

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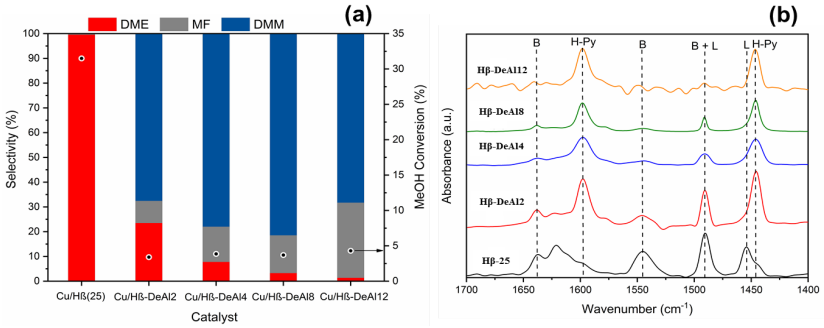

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In-situ synthesis of SAPO-34 on γ-Al_2O_3 microspheres: a suitable fluidized-bed catalyst for methanol conversion to light olefins

Ghavipour, M.[1], **Kopyscinski, J.** [1,*]

Chemical Engineering Department, McGill University, 3610 University Street, Montreal, Canada
**jan.kopyscinski@mcgill.ca*

Introduction

Considering the environmental regulations and concerns, researchers have focused on developing green technologies based on a closed-loop carbon cycle. This, for instance, can be done by steam-reforming or partial oxidation of plastic wastes to synthetic gas, which in turn will be converted to methanol and subsequently to light olefins for plastic production. Methanol conversion to light olefins (MTO) is a key step within this cycle and recently has attracted researchers' attention [1]. Narrow-pore silica aluminum phosphate (SAPO-34) is known as the optimum catalyst for the MTO reaction with complete methanol conversion and over 80% light olefin selectivity. The only drawback is the fast catalyst deactivation due to coke formation, which is why a fluidized-bed reactor with continuous regeneration is employed.

Hydrothermally synthesized SAPO-34 zeolite has cubic particles with a size range of 1-5 μm (Fig 1 left) whereas, for the fluidized-bed application, particles of 50-100 μm are required. The traditional spray-drying method cannot be employed as the microporous structure of the SAPO-34 catalyst tends to be blocked by the binder and its physicochemical properties will be affected negatively. Our aim here is to develop a synthesis method in which SAPO-34 particles are synthesized on γ-Al_2O_3 microspheres. By employing this method, the precious SAPO-34 particles will not bury in the middle of the agglomerates, instead, they will be in the outer layer accessible to the reactants. To adhere the SAPO-34 particles to the support, the alumina precursor required for SAPO-34 preparation would be provided from the γ-Al_2O_3 microspheres' outer surface.

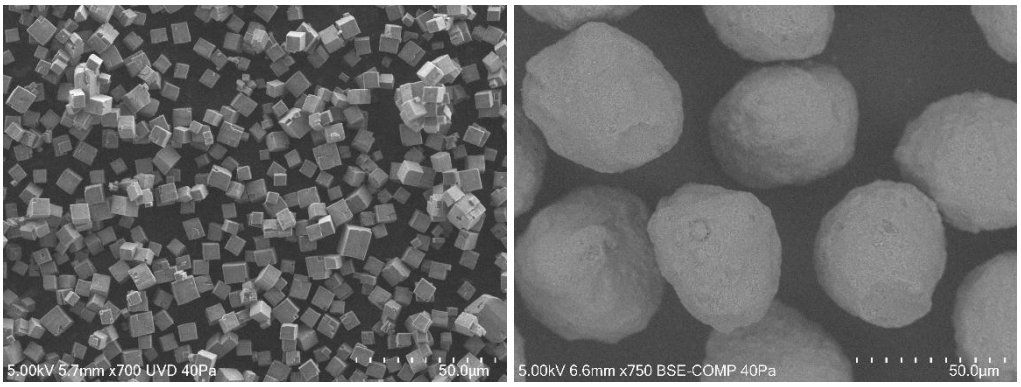

Fig 1 SEM images of left) as-synthesized cubic SAPO-34 crystals, right) bare γ-Al_2O_3 microspheres

Materials and Methods

SAPO-34 was hydrothermally synthesized on γ-Al_2O_3 microspheres (dry support/gel mass ratio of 0.4) with mixed-template (TEAOH and DEA). Activity tests were performed in a fixed-bed microreactor at 420°C, atmospheric pressure, and WHSV of 1 h^{-1}. Different synthesis procedures and treatment methods were employed to activate the outer layer of the γ-Al_2O_3 microspheres and fully cover it with the SAPO-34 phase.

Results and Discussion

While keeping the microspheres intact, the outer layer of alumina was activated successfully to react with other precursors to form the SAPO-34 outer shell. Comprehensive catalyst characterization tests (such as XRD, BET, SEM, SEM-EDX, NH_3-TPD, and TGA techniques) were employed to characterize the supported catalyst. Activity tests (based on the SAPO-34 content of the supported catalyst) were conducted and the results showed that the catalyst lifetime and product distribution are similar to those of pure unsupported SAPO-34. The supported catalyst underwent an abrasion test in a simulated fluidized-bed chamber for 10 days while monitoring the catalyst's weight loss and morphology. The results indicated good mechanical strength of the developed catalyst. In conclusion, the in-situ SAPO-34 synthesis over γ-Al_2O_3 microspheres seems to be an effective catalyst for the fluidized-bed reactor application.

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Phosphorus deactivation of cobalt-based catalysts for Fischer-Tropsch synthesis

O. Ivanez Encinas[1*], A. San Martin[1], E. A. Blekkan[1]

[1] *Norwegian University of Science and Technology (NTNU), Department of Chemical Engineering, Sem Sælands vei 4, 7491, Trondheim, Norway*
[*] *Oscar.l.i.encinas@ntnu.no*

Keywords: Fischer-Tropsch, Biomass to liquids, cobalt, poison.

Introduction. Biomass to liquids (BTL) via gasification and Fischer-Tropsch synthesis (FTS) is an interesting technology for fuels and chemicals production. With the use of biomass comes the opportunity to use waste as feedstock and improve efficiency of different industries while reducing the CO_2 emissions. However, there are several challenges to overcome to do BTL feasible. One of the most important is the syngas gas cleaning before further utilization. Biomass has a wide range of inorganic species [1] that will end up as volatiles in the gas phase after the gasification [2]. There have been several studies [3] regarding the effect of the most common species present in biomass as S, alkali metals, nitrogen compounds in the FTS. However, phosphorus has not received much consideration. In this context, our study is focused on test the effect of the addition of phosphorus to cobalt-based catalysts in the FTS.

Experimental/methodology. Three different cobalt-based catalysts supported on Al_2O_3, TiO_2 and SiO_2 were prepared by incipient wetness impregnation. To screen the effect of phosphorus in the catalysts, different loadings of phosphorus were added to the catalysts, from 1700 to 6700 ppm. The catalysts were characterized by TPR, N_2 adsorption-desorption, H_2 chemisorption and XRD. The FTS was performed in a tubular fixed bed reactor with 1g of catalyst and 19g of SiC; at 240 ºC and 5 bar.

Results and discussion. The activity of the catalysts was compared in by CO conversion and site-time yield during the first 24 h. After this time, the CO conversion was adjusted to 50 % to compare the selectivity. In Figure 1, it is depicted the CO conversion during the first 24 h on stream for the cobalt catalysts supported on Al_2O_3, TiO_2 and SiO_2.

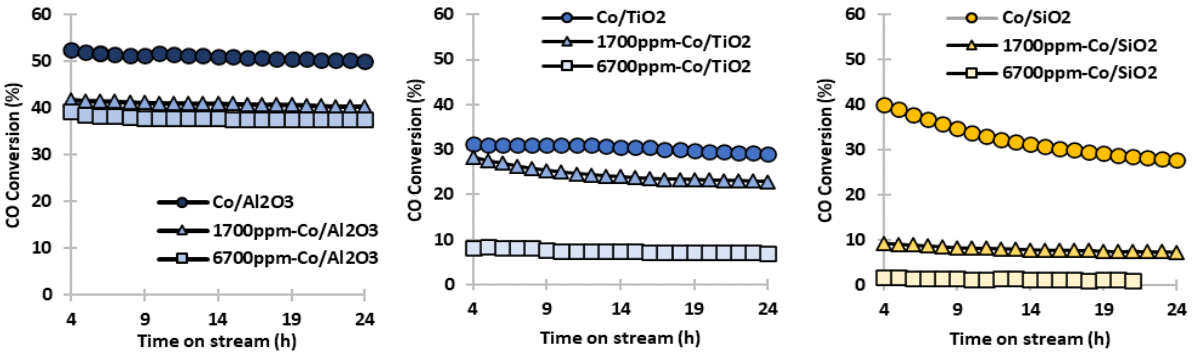

Figure 1: Effect of P on the CO conversion during the first 24 h on stream for the cobalt catalysts. Left: Supported on Al_2O_3, centre: supported on TiO_2 right: supported on SiO_2.

The addition of phosphorus led to a small decrease in metallic dispersion as well as a decrease in cobalt reducibility. Furthermore, this contamination reduced the activity of the catalysts in different degrees. In the case of Al_2O_3 support, the deactivation was less pronounced compared to TiO_2 and SiO_2, to the extent that both catalysts showed no activity with the higher P loading. This difference might be due to different metal-support interactions. Regarding the selectivity, it was affected by the poisoning of P with an increase in methane and paraffins while reducing the light olefins and C_{5+} products.

Acknowledgments

We are grateful to The Norwegian Research council for funding through contract nº 257622.

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Advancing high-yield strategies for methane partial oxidation to methyl derivatives with heterogeneous catalysis

A. Blankenship[1], Y. Ji[1], M. Ravi[1], M. Newton[1], J.A. van Bokhoven*[1,2]

[1]*Institute for Chemical and Bioengineering, ETH Zurich, Zurich, Switzerland*
[2]*Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute, Villigen, Switzerland*
[*]*jeroen.vanbokhoven@chem.ethz.ch*

Keywords: heterogeneous catalysis, methane partial oxidation, esterification, manganese, cobalt

Introduction. The direct partial oxidation of methane to primary oxygenates such as methanol suffers from impractically low product yields due to the facile over-oxidation of the desired product to CO_2 under the reaction conditions necessary for methane activation [1-3]. Protecting methanol within a less reactive, oxidation-resistant methyl ester is an effective product protection stratety that breaks through this selectivity-conversion trade-off, thereby obtaining high methane-based yields and product concentrations [1, 4]. Despite the high yield and productivity of methane-to-methyl-ester systems, there are a number of critical shortcomings left unaddressed that preclude their practical applicability, including: the reliance on molecular Pt-group catalysts, economically infeasible oxidants (e.g. $K_2S_2O_8$), and the use of corrosive, fully concentrated acid solvents [5].

Experimental/methodology. Cobalt and manganese precursors were deposited on various oxide supports (SiO_2, Al_2O_3, TiO_2, etc.) via incipient wetness impregnation and liquid deposition. The catalyic performance was screened in a stirred batch reactor with a diluted TFA mixture at 215°C (described in [6] in detail). Metal leaching and homogeneous contributions to activity were evaluated through ICP and hot filtration of the reaction filtrates. Solid catalysts were characterized using various methods (e.g. XRD, TEM, BET, XAS etc.).

Results and discussion. In this work, we introduce a number of improvements to methane-to-methyl-ester systems that alleviate some of the major shortcomings in catalysts, oxidants, and the acidic reaction medium. Importantly, we report the first heterogeneous catalysts for this reaction that are compatible with O_2 as a terminal oxidant and do not utilize Pt-group metals. Under our improved reaction conditions, Co/SiO_2 and Mn/TiO_2 display competitive performance on the basis of turnovers and ester production rates (up to 245 and 613 μmol g_{cat}^{-1} h^{-1}, respectively) in comparison to previously reported, homogeneously-catalyzed systems that employ stronger oxidants and higher methane partial pressures. The metal leaching and homogeneous contributions from these catalyst were neglible, confirming the heterogeneous nature of the catalysis. Furthermore, we find that high metal dispersion is associated with high activity in this system, and the most efficient utilization of cobalt or manganese is realized at the lowest loading. Through a combination of characterization techniques, correlaitons between catalytic activity and the presence of specific metal species present in the catalyst can be derived. The conclusion of the contribution underscores impactful directions for the further development of high-yield methane conversion processes through more holistic consideration of catalysts, reagents, and operating conditions, with a focus on current work toward a novel continuous flow system for methane-to-methyl-ester chemistry.

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Significant enhancement of coking resistance in partial oxidation of methane over Fe-doped Ni/γ-Al_2O_3 catalysts

A. Khaleel*, A. Pillantakath, A. Adamson

Department of Chemistry, United Arab Emirates University, Al-Ain, UAE
**abbask@uaeu.ac.ae*

Keywords: Methane, partial oxidation, Ni catalysts

Introduction. While different catalytic routes have been studied for CH_4 conversion to more efficient feedstocks, partial oxidation has been widely investigated as a potential and promising route due to advantages that include its exothermic reaction, and producing syngas in high yields with a H_2/CO ratio very close to 2, as desired for gas-to-liquid technology [1,2]. While the most active catalysts for these processes are based on expensive noble metals, Ni-based catalysts have attracted significant attention due to their abundancy and lower costs [3]. However, the reaction over most of the studied catalysts, to date, suffer major drawbacks including catalyst's sintering and coke formation.

In the present study, Ni/γ-Al_2O_3 catalysts were modified by incorporating Fe^{3+} ions in the bulk of the support to introduce redox functionality to enhance coke oxidation and removal. The results revealed that Fe ions in the support resulted in textural modification and a significant enhancement of the catalyst coking resistance.

Experimental. Fe-doped γ-Al_2O_3 was prepared via a sol-gel method using aluminum sec-butoxide and Fe(III) nitrate in 2-propanol. Ni catalysts with 10 wt% Ni loading were prepared by wetness impregnation method followed by calcination at 700 °C. Catalysts were prepared in Fe/Al+Fe molar ratio in the range of 0.01-0.15, which will be referred to as Ni/FeX where X represents the molar ratio (Fe/Al+Fe) x 100. The catalysts were characterized by various techniques including, XRD, XPS, HR-TEM, N_2-sorption, H_2-TPR, CO_2- and NH_3-TPD, TGA, and Raman spectroscopy. Catalytic activity tests were conducted at 700 °C and 1 atm using a continuous-flow fixed bed reactor. The reaction feed was composed of CH_4 (30%), O_2 (15%) and N_2 (55%) with a total flow rate of 50.8 mL min^{-1}.

Results and discussion. Concentrations of Fe(III) as high as 10% could be well dispersed in the alumina matrix while higher concentrations promoted the formation of the binary oxide phase, $NiFe_2O_4$, which upon reduction resulted in the formaiton of $FeAl_2O_4$. The catalysts with Fe(III) concentrations of 1-5% exhibited a significant enhancement in coking resistance during partial oxidation of methane to synthesis gas, where negligible amounts of crystalline carbon formed and stable performance was exhibited during 100 hrs on-stream. The significantly enhanced coking resistance was referred to the role Fe^{2+} ions, that were found to be the dominant iron state upon reduction, in a possible redox cycle that promoted the oxidation of carbon preventing its accumulation on the catalysts. In addition, the presence of the iron in the support enhanced the γ-phase stability and was associated with enhanced catalysts' porosity, which has contributed to the removal of carbonaceous species by enhancing internal mass diffusion. The results of this study hold a great promise for developing robust and durable catalytic materials for methane reforming.

Acknowledgments
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High performance of Fe-Mn/Nb_2O_5 catalysts in the Fischer-Tropsch Synthesis

H. S. T. Silva[1*], D. P. S. Silva[1], G. G. Silva[2], A. G. M. Silva[1], R. R. Soares[1]

[1]*Faculty of Chemical Engineering – Federal University of Uberlandia – Brazil, Uberlândia, MG.*
[2] *Institute of Chemistry – Federal University of Uberlandia –Brazil, Uberlândia, MG.*
**hidila@ufu.br (corresponding author)*

Keywords: Fe-Mn catalysts, Mesopourous Nb_2O_5, Fischer-Tropsch Synthesis, Low CO_2, High C_{5+} and $C^=/C^-$

Introduction.

Fischer-Tropsch Synthesis (FTS) has been growing interest due to its relevance on providing biofuels such as biojet and green diesel. Catalysts promoted with manganese can favor the growth of the carbon chain, in addition to generating products with greater added value [1]. Thus, this work has designed, characterized and evaluated the performance of Fe promoted with Mn catalysts on mesoporous niobia in the FTS.

Experimental/methodology.

Iron (15 wt.%) was deposited on mesoporous niobia by wet impregnation and precipitation-deposition methods [2]. Then they were dried overnight and calcined at 400°C at 5°C/min before adding manganese (1, 3 and 5% wt%) by incipient wetness impregnation followed the same drying and calcination procedures. The catalysts were characterized by N2-physisorption, H_2 and CO-TPR, MEV, DRS-UV-Vis, XRD, Mossbauer, and CO-TPD. The Fischer-Tropsch reaction was carried out in a stainless-steel fixed-bed reactor. The catalyst (400 mg) was mixed with quartz sand (400 mg) and then reduced in situ using high purity H_2 at 400 °C, time in flow=12h, and atmospheric pressure. After reduction, the catalytic tests were carried out at 20 bar, 250-300 ºC and GHSV 500-1500 h^{-1}, TOS=30 h and H_2/CO ratio=1 and 2.

Results and discussion.

The selectivity and conversion of the catalysts applied in the SFT at 250 ºC, 20 bar, and 500 h^{-1} of GHSV are shown in Figure 1. The selectivity for the products obtained in the SFT demonstrates that the presence of manganese as a promoted phase in an iron catalyst reduces the formation of methane (from approximately 25% in 15Fe/Nb2O5m to approximately 12% in 3Mn-15Fe/Nb_2O_5m) and carbon dioxide. In addition, there was a greater selectivity for heavy hydrocarbons (C_{5+}). It is noted that the CO conversion is reduced at low and high Mn concentrations, indicating that this metal significantly influences the obtaining of the desired products and the olefin/paraffin ($C^=/C^-$) ratio. The characterization results demonstrated that oxycarbides are formation are responsible of the catalytic performance evolution.

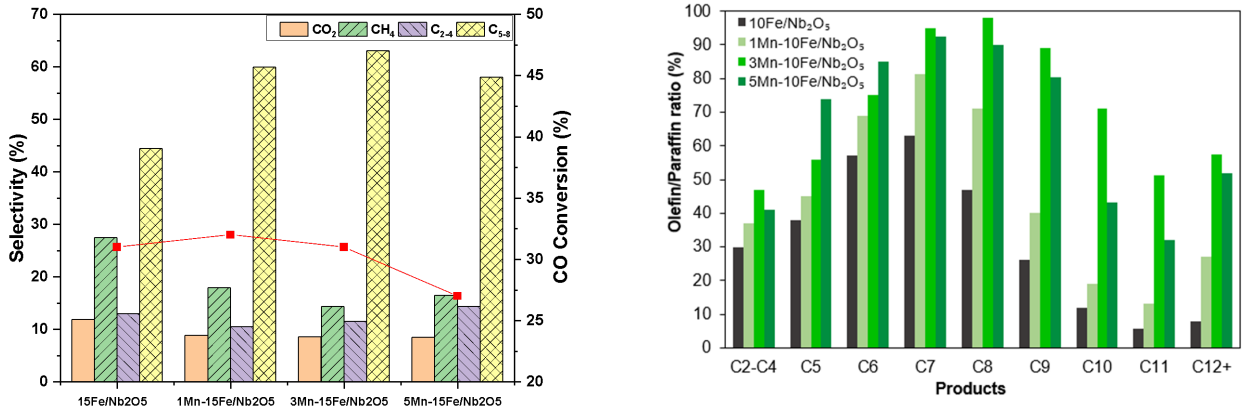

Figure 1. CO conversion, selectivity and olefin/paraffin ratio under Fe-Mn/Nb_2O_5 catalysts in the FTS at 250 ºC, 20 bar, and GHSV=500 h^{-1}.

Acknowledgments

We are in debt with FAPEMIG, CAPES, CNPq, PETROBRÁS, SUZANO,EMBRAER, and KLABIN for the finantial support

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Effect of CO_2 content in feed gas mixture for Fischer-Tropsch Synthesis over Co/SiO_2 catalyst

S. Satokawa*, N. Wachi, H. Konno, A. Yanagita, K. Tashiro

[1] *Seikei University, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo 180-8633, Japan*
satokawa@st.seikei.ac.jp

Keywords: Fischer-Tropsch synthesis, Co/SiO_2 catalyst, CO_2 content

Introduction.

Technology for synthesizing liquid fuels by CO_2 hydrogenation has attracted attention toward the realization of carbon neutrality. This can be achieved by combining the reverse water gas shift (RWGS) reaction, which converts CO_2 to CO, and the Fischer-Tropsch synthesis (FTS) reaction, which converts CO to hydrocarbons. Here, since the former RWGS reaction is governed by thermodynamic equilibrium, the ratio of CO and unreacted CO_2 contained in the exit gas (CO/CO_2) depends on the reaction temperature. Therefore, the FT catalyst in the latter stage is required to have the performance of selectively reacting only CO even under the condition that CO_2 is contained in the reaction gas [1]. In this study, we conducted an activity test of the FTS reaction over Co/SiO_2 catalyst with mixed gases containing CO and CO_2 of various compositions. In addition, effects of reaction temperature, pressure, and H_2/CO_x mixed ratio were also conducted.

Experimental

$Co(20wt\%)/SiO_2$ catalyst was prepared by impregnation method. An aqueous solution containing cobalt (II) nitrate hexahydrate was added to a commercially available SiO_2 carrier (CARiACT Q-10, Fuji silysia chemical), and mixed in a mortar for 20 min. Then, it was dried overnight at 110 °C and calcined in the air at 400 °C for 6 h. The FTS activity test was carried out using a high pressure fixed bed flow reactor. First, a mixed gas of H_2/N_2 = 1/4 was passed at 50 mL min^{-1} at 350 °C for 2 h to reduce the catalyst. After that, under the conditions of 220 °C, 1.0 MPa, and H_2/CO_x = 2-3, feed gases with different CO/CO_2 ratios were flowed at 60 mL min^{-1}. The obtained gas was analyzed with a gas chromatograph (MCGC990, agilent), and the liquid components were collected with a gas-liquid separator and then analyzed with a gas chromatograph mass spectrometer (GCMS-QP2010, shimadzu).

Results and discussion

Fig. 1 shows the CO_x conversions and product selectivities in the feed gas with different contents of CO and CO_2 at 220 °C and 1.0 MPa. The COx conversion in the case of mixed gas condition was higher than those with synthesis gas and CO_2 mixed gas ($CO_2/(CO_2+CO)$ = 0 and 1.0) conditions. In addition, it was found that the COx conversion rate and the methane selectivity increased as the CO_2 concentration in the mixed gas increased. The selectivity and yield of the liquid hydrocarbons (C_{5+}, others) were maximum at $CO_2/(CO+CO_2)$ = 0.3 and 0.5, respectively. CO_2 was not consumed during the FTS reaction using the mixed gas feed. Therefore, when CO and CO_2 are mixed in an appropriate ratio, the efficiency to obtain the liquid fuel increases.

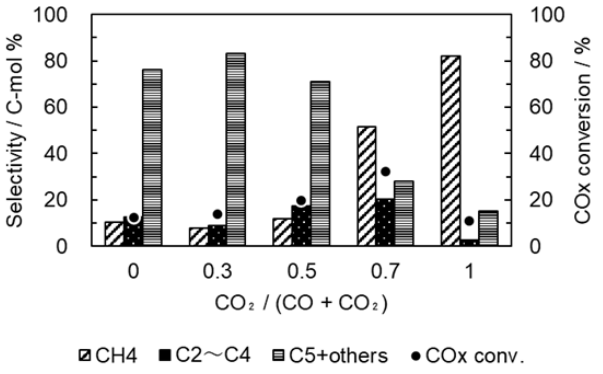

Fig. 1 Effect of CO and CO_2 mixed ratio for FTS reaction activity over Co/SiO_2 at 220 °C and 1.0 MPa.

Acknowledgments

This study has been conducted under a contract with the New Energy and Industrial Technology Development Organization (NEDO), Japan. We would like to express our gratitude to NEDO.

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Direct conversion of carbon dioxide into liquid fuels and chemicals by coupling green hydrogen at high temperature

Yubing Li, Kang Cheng*, Qinghong Zhang, Ye Wang

State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

**Corresponding Author:* kangcheng@xmu.edu.cn

Keywords: Zeolite; liquid fuels; chemicals; CO_2 reduction; bifunctional catalysis; hydrogen storage

Introduction. The growing environmental concerns and increasing demand for carbon feedstocks have stimulated recent research activities on the transformation of CO_2. Bifunctional catalysis opens a new strategy for the selective hydrogenation of carbon dioxide (CO_2) into hydrocarbon fuels and chemicals using green hydrogen, which not only utilizes abundant CO_2 as a carbon feedstock but also enables the storage of hydrogen.[1] In this work, we investigate the direct hydrogenation of CO_2 to gasoline-range hydrocarbons and olefins over a series of bifunctional iron-zeolite catalysts operated at high temperatures (> 300 °C).[2] This process may efficiently utilize CO_2 discharged from industrial combustion and green H_2 produced by high-temperature solid oxide electrolytic cells (SOEC).

Experimental/methodology. Iron oxides promoted by a series of alkaline metals were synthesized by a sol-gel method. H-SSZ-13, H-MOR, H-Beta, H-Y, H-ZSM-35, H-MCM-22, H-ZSM-22, H-ZSM-5 and H-ZSM-48 were commercial products. The iron oxides and zeolites were integrated with different proximity.

Results and discussion. The bifunctional catalysts, composed of FeMnK oxide and nine zeolites with different topologies, have been investigated for CO_2 hydrogenation at high temperatures. FeMnK+H-ZSM-5 offered a 70% selectivity of C_5–C_{11} hydrocarbons together with a 17% selectivity of C_2–C_4 olefins (Fig. 1). A volcano trend was obtained between the pore size of zeolites and the selectivity of C_5–C_{11} hydrocarbons. The 10MR zeolites favored the formation of C_5–C_{11} hydrocarbons, while both 8MR and 12MR zeolites could not promote the C–C chain growth. As the temperature increased from 320 °C to 400 °C, CO_2 conversion increased significantly from 32% to 51% while CO selectivity was kept at low levels of around 15%. Besides, the yield of aromatics increased more than doubled over the FeMnK+H-ZSM-5 catalyst. Moreover, the key factors determining the catalytic performances, dynamic evolution of active sites, and reaction network have been intensively investigated and clarified.

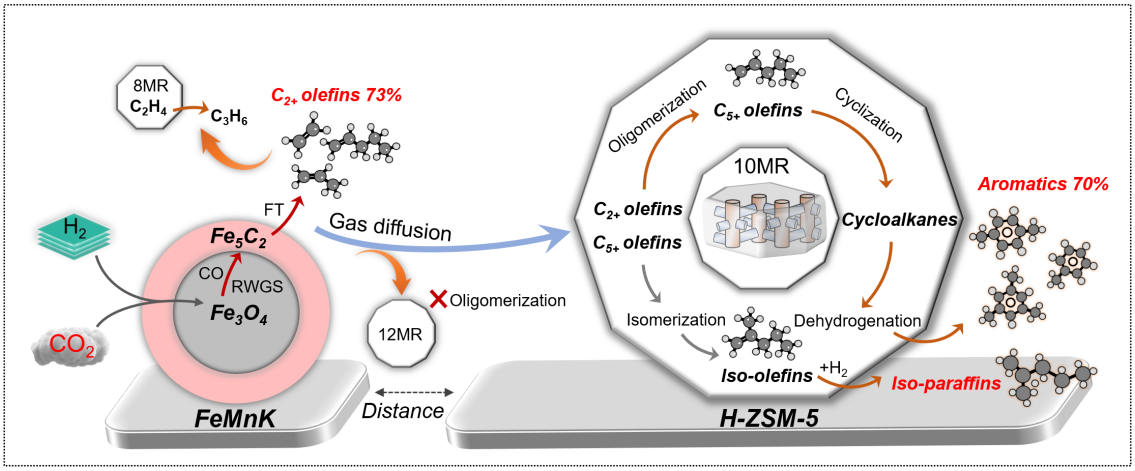

Fig. 1. Reaction mechanism for CO_2 hydrogenation over FeMnK+Zeolite bifunctional catalysts.

Acknowledgments

This work was supported by the National Key Research and Development Program of MOST (No. 2019YFE0104400), and the National Natural Science Foundation of China (Nos. 91945301, 22121001, and 22222206).

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Methylation of light alkenes and aromatics though step-wise reaction with methane in Cu-exchanged Zeolites

B. G. Solemsli[1], S. Prodinger[1], K. Kvande[1], G. Deplano[2], U. Olsbye[1], S. Bordiga[2], P. Beato[3], S. Svelle*[1]
[1] *SMN Centre for Materials Science and Nanotechnology, Department of chemisty, Univerisy of Oslo, Oslo, Norway*
[2] *Department of Chemistry, NIS and INSTM Reference Centre, University of Turin, Turin, Itally*
[3] *Haldor Topsøe A/S, Kongens Lyngby, Denmark*
* *stian.svelle@kjemi.uio.no*

Keywords: Methane, Zeolites, Copper, Partial Oxidation, Methylation, Alkenes, Aromatics

Introduction.

Direct partial oxidation of methane into methanol (DMTM) has been in the focus in research for the chemical industry for several decades. Copper exchanged zeolites have shown potential for this by utilizing a chemical looping protocol [1-3]. Zeolites have also been utilized as catalysts for the Methanol-to-hydrocarbons (MTH) reaction [4]. By combining the DMTM and the MTH reactions, hydrocarbons can be synthesized directly from methane, limiting the scale and the cost for industrial processes.

Among the most promising zeolites for DMTM is the mordenite (MOR) type, while ZSM-5 has long been utilized for the MTH reaction [1,5]. In this study, Cu-, Na-exchanged and protonated MOR, ZSM-5 and CHA zeolites were tested for the step-wise methylation of ethylene, propylene and benzene.

Experimental/methodology.

Tests were carried out with a laboratory scale gas feed reactor set-up, with the effluent being analyzed by an online MS and quantifications done with a GC FID. By varying sample composition, zeolite framework type and reaction conditions, screening of methylation reactions was carried out. The reaction protocol consisted of three steps: oxidation of the Cu zeolite at 773 K in O_2, activation of methane at 473 K and extraction with either 100% ethylene, 100% propylene or 10% benzene/He at 473 K. All samples were characterized, both before and after testing.

Results and discussion.

Results suggest that two separate reactions occur when the adsorbed methoxy species are extracted with ethylene: methylation forming propylene, and oligomerization and cracking yielding a mixture of C_4-C_7 hydrocarbons. Extraction with propylene revealed that the same two competing reactions occurred. However, a higher affinity towards the oligomerization reaction was seen, with C_6 as the main product. The sample showed signs of coke formation after reaction, that could be burned off afterwards.

Benzene methylation yielded only toluene. The toluene yield was about 40 % relative to the yield of methanol observed with steam extraction. The MOR framework was the most active, while CHA framework did not show any activity.

The lower amount of toluene produced indicates that not all the methoxy species formed when activating methane can be accessed by the large benzene molecule. Benzene cannot enter the CHA pores, and will be highly restricted in the 8 rings of MOR. This might give a new insight into how the methoxy species behave inside the zeolite framework during the reaction.

Acknowledgments

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Investigation of the deactivation mechanism of iron-based catalysts for use in low-temperature Fischer-Tropsch-Synthesis

Sascha Bredow[1*], Erik Reichelt[2], Matthias Jahn[3]

[1]*Fraunhofer IKTS, Dresden, Germany*
[2] *Fraunhofer IKTS, Dresden, Germany*
[*]*Sascha.tim.bredow@ikts.fraunhofer.de*

Introduction

Depending on the applied catalytic material Fischer-Tropsch-Synthesis (FTS) can be used to produce short and long-chained hydrocarbons and oxygenates. Compared to cobalt-based catalysts iron-based catalysts have the advantage of higher selectivity towards oxygenates and especially higher alcohols[1] which are linear 1-alcohols with a chain length of more than four carbon atoms. The synthesis of higher alcohols via a sustainable pathway is of high interest since they are a demanded industrial product. Utilizing sustainably sourced syngas in FTS an alternative green route to higher alcohols could be achieved[2].

Responsible for the catalytic activity of those FT catalysts are numerous iron carbides which is generally agreed upon in the scientific community[3]. However their chemistry is not yet fully clarified, even though iron-based catalysts are becoming more and more attractive for research and industrial applications[1,3]. Studies concluded that different carbide phases influence FT activity and are able to shift the product composition[4,5]. In addition the composition of iron-based catalysts is known to change during FT synthesis due to mainly four different deactivation mechanisms[1,6]. Because of this complex and dynamic nature of the iron carbide phases and their composition on the catalyst surface make it challenging to find correlations between the catalyst performance and its composition[3].

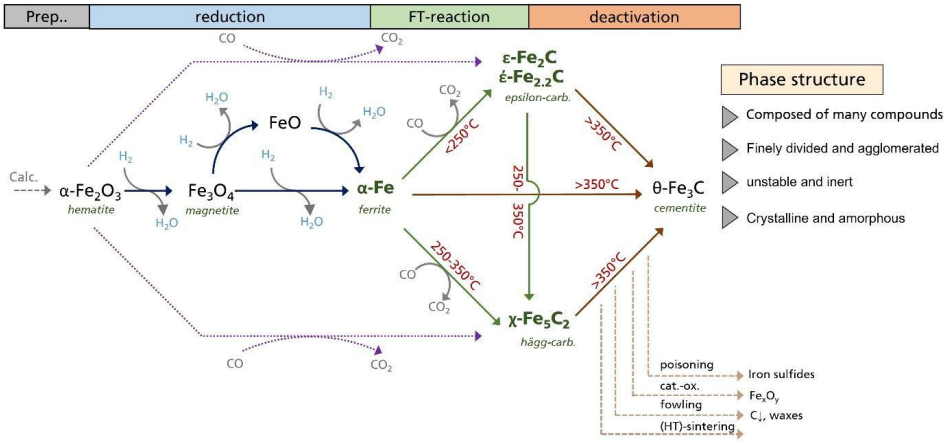

Figure 1 - Evolution of iron phases in FT catalysis (adapted from de Smit et al.[4])

Experimental/methodology.

In order to elucidate the not yet fully known connections between catalyst performance, phase composition and the associated degradation behavior it is purposeful to synthesize phase-pure iron carbide catalysts. These catalysts are then exposed to syngas under FT conditions and their phase composition as well as the yielded product spectrum are analyzed at different stages of the reaction. For that purpose, also accelerated aging is a valuable tool. According to this approach it should be possible to investigate the deactivation behavior of different iron carbide phases. Furthermore, it could give insight into the individual catalytic activities of different carbide materials, especially regarding their influence on product distribution.

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Cobalt-based Fischer-Tropsch Synthesis catalysts for the conversion of CO_2-rich syngas

B.C.A. de Jong[1], H.H. van de Bovenkamp[1], G. Boer[1], L. Rohrbach[1], G. L. Bezemer[2], H.J. Heeres and J. Xie[1*]

[1]*Green Chemical Reaction Engineering, Engineering and Technology Institute Groningen, University of Groningen, Groningen, The Netherlands*

[2] *Energy Transition Campus Amsterdam, Shell Global Solutions International B.V., Grasweg 31, 1031 HW Amsterdam, The Netherlands*

[*] *corresponding author: jingxiu.xie@rug.nl*

Keywords: Fischer Tropsch Synthesis, catalysis, cobalt, CO_2, clean fuels.

Carbon capture and conversion of industrial flue gasses into aviation fuel range hydrocarbons is an appealing technology considering the large energy demand of the aviation sector and the few available alternatives [1]. The conversion of CO into long chain hydrocarbons over cobalt-based catalysts has been extensively investigated, but the conversion of CO_2 over these type of catalysts produces mainly methane [2]. Industrial flue gases e.g. typical steelwork off-gases are mainly composed of CO, CO_2, H_2 and N_2 and therefore a reverse water gas shift and gas separation step would be needed to convert these flue gases into synthesis gas [3]. However, if the Fischer Tropsch process would be tolerant for CO_2, a one-step conversion of flue gas into long chain hydrocarbons could be achieved. The performance of cobalt-based catalysts for mixed feed Fischer Tropsch is debated as some research claims the CO_2 to be an inert whereas others claim the CO_2 to be hydrogenated into methane along with the CO [4,5]. Surprisingly when a 50/50 CO_2/CO feed was used over a cobalt on titania P25 catalyst a C_{5+}-selectivity of almost 80 % could be achieved. These results are difficult to compare with state-of-the-art literature because in mixed feed experiments, the ratio of H_2/atomic carbon is often different which affects the conversion level and besides, an increase in CO_2 content changes the H_2/CO ratio which affects the CO conversion as well [6]. In Figure 1, the C_{5+}-selectivity versus CO outlet partial pressure is given for various H/atomic carbon ratios and with a sufficient CO-partial pressure available, a high C_{5+}-selectivity can be achieved. In this work the CO conversion level and hence the CO outlet pressure is tuned for different CO_2/CO mixtures by varying the GHSV. Based on these results, the highest possible CO_2-concentration in a mixed feed Fischer-Tropsch process for the efficient production of synthetic aviation fuels is determined.

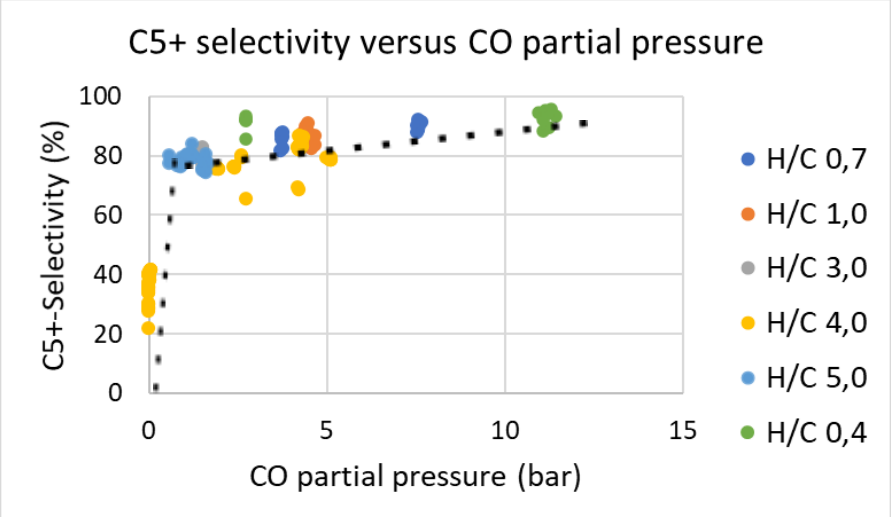

Figure 1 C_{5+}-selectivity versus CO partial pressure in the outlet for various CO and CO/CO_2 Fischer Tropsch experiments with varying H_2/atomic carbon ratios. The reactions are performed in a PBR at 220°C 20 barg with argon as internal standard.

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[*]*Corresponding Author's E-mail address (Calibri, 11 pt., Italic)*

Keywords: (optional, Calibri, 11 pt.) keyword 1, keyword 2, keyword 3…
Introduction. The text should be 11-point Calibri.
Experimental/methodology. The text should be 11-point Calibri.
Results and discussion. The text should be 11-point Calibri. Figures and tables can be embedded in this section. Caption (Calibri, 10 pt., Bold) should be given below the figures & above the tables.

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[1] Makadia, H.K.; Siegel, S.J. *Polymers* **2011**, *3*, 1377-1397.
[2] Siqueira, G. et al. *Polymers* **2010**, *2*, 728-765.

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Bench-scale FT crude production from CO_2 using a two-step rWGS-FT process

Author's Name: Christian Frilund[1], Pekka Simell[1]

[1]VTT Technical Research Centre of Finland, Espoo, Finland

Keywords. CPOX, rWGS, Fischer Tropsch, P2X

Introduction. Catalytic reverse water-gas shift (rWGS) has the potential for high volume CO_2 valorization to chemicals. With the use of renewable hydrogen and CO_2 in for example power-to-X applications rWGS unlocks a wide range of syngas reactions, inlcuding Fischer Tropsch (FT) synthesis for the fossil-free production of hydrocarbons. The thermodynamics show that for feasible CO_2 conversions very high reaction temperatures are required, for which the heat can be either supplied directly or indirectly. In this research, the focus is on a two-step CO_2 to FT process where the FT off-gases (unreacted H_2,CO, CO_2 and C1-C5) are re-circulated to an rWGS stage with oxygen feeding (in-situ combustion) and hydrocarbons reacting by catalytic partial oxidation (CPOx). Here we present results of a bench-scale implementation of this coupled 2-stage process concept.

Experimental/methodology. A compact tubular CPOx/rWGS reactor was constructed, consisting of an in-house prepared noble-metal catalyst coated on FeCrAl monoliths, designed to be operated at FT pressure (up to 20 bar) and high temperature (up to 900 C). The process was downstream coupled to an existing bench-scale FT process, including FT gas reciruclation to the CPOx/rWGS stage. Industrial-grade bottled gases were fed to the CPOx/rWGS using thermal MFCs. Gas analysis was performed using a TCD/FID-GC. Condition screening factorial tests were designed using MODDE Pro software. Thermodynamic equilibrium calculations were performed using HSC Chemistry.

Results and discussion. *Standalone CPOx/rWGS tests.* The CPOx/rWGS reactor outlet gas composition was compared to the equilibrium gas composition. The results are shown in Figure 1.

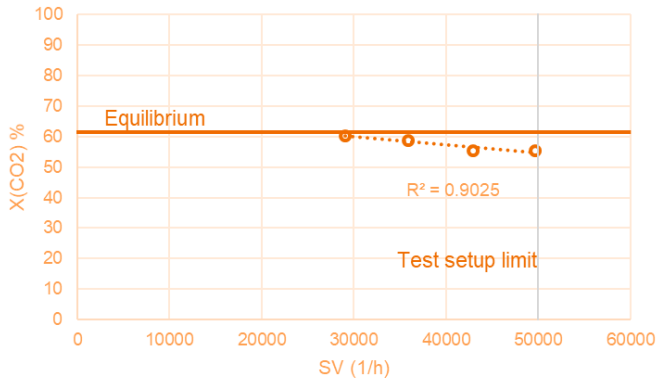


Figure 1. CO_2 conversion as a function of gas hourly space velocity.

At around SV 30 000 1/h the thermodynamics predicted equilibrium gas composition in the outlet is almost fully achieved. Even at SV 50 000 1/h the output gas has not drifted far from the equilibrium, thus verifying that rWGS can be performed at high throughput conditions. Condition screening is performed using a 4 factor and 2 level experimental design, with controlled factors reaction temperature, CO_2 feed rate, feed H_2/CO_2 ratio and reaction pressure. The condition screening highlighted the effect of a higher H_2/CO_2 leading to a higher CO_2 conversion, but also higher methane (methanation) selectivity. A higher reaction temperature promoted the formation of CO instead, both in terms of a higher CO selectivity as well as higher CO_2 conversion.

Coupled CPOx/rWGS tests. Extended duration coupled CPOx-FT tests with an approximately 20 % recycle ratio were performed. The results showed that the CPOx/rWGS is able to fully decompose C2+

hydrocarbons, but a very small C2 portion remained in the outlet gas. The system was operated for over 300 h (non-continuous) with an average specific activity of 300 mmolCO/cm^3cat*h.

Balancing between OCM catalyst deactivation and activity through design and controlled composition

Baoting Huang, Jin Wang, Dina Shpasser and Oz M. Gazit*

[1]*Technion - Israel Institute of Technology, Haifa, Israel*
**ozg@technion.ac.il*

Keywords: La_2O_3, Na_2WO_4,

Introduction. The Mn-Na_2WO_4/SiO_2 (MnNaWSi) catalyst for the oxidative coupling of methane (OCM) has been and still is regarded as the most promising catalyst for OCM with reports showing CH_4 conversion ~25% with a C_2 selectivity of ~80% (@ >800 °C) over long periods of time. Despite the remarkable performance of the MnNaWSi catalyst, recent reports show that structural changes and deactivation in the multi-metal oxides material occur under reaction condition.[1,2] Distinctly it is the melting of crystalline Na2WO4 at 698 °C that is believed to impose instability in the catalyst structure due to its strong interaction with the silica support and the MnOx phase as well as its evaporation at the high reaction temperature.

Experimental/methodology. The catalysts were tested using a single-pass fixed-bed flow reactor made of quartz with an inner diameter of 7 mm. In each run of reaction, 50 mg of catalyst was loaded and packed inside the reactor. Two pieces of quartz wool were loaded and packed on both ends of the catalyst bed like a sandwich configuration to stabilize the reactor bed. Prior to catalyst loading the sample was sieved and collected within 60-100 mesh. The reactor bed was packed to be consistently 5 mm long. The feed gas composition and flowrate were controlled by mass flow controllers (Brooks SLA5850). Typically, the feed gas mixture had a total flow of 50 ml min^{-1} STP with composition of 4:1:1:4 CH_4:O_2:N_2:Ar, which results in GHSV (gas hourly space velocity) of 60,000 ml h^{-1} g^{-1}.

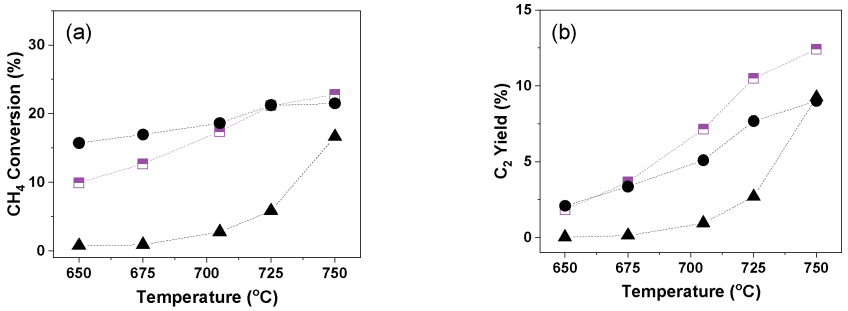
Results and discussion. we the demonstrate the promotion of OCM over a two-domain catalyst bed composed of a La_2O_3/MgO catalyst and the MnNaWSi catalyst. We show that the OCM mechanism is promoted by the synergistic interactions between the two catalysts when the former is stacked on top of the latter. Our results show that a catalyst bed composed of 10 wt% La/MgO stacked on-top of 90 wt% MnNaWSi (La/MgO-MnNaWSi_0.1s) is able to give ~10% methane conversion and ~19% C_2 selectivity at ~650 °C, whereas at the same temperature the MnNaWSi is inactive and the La/MgO gives only 13% selectivity. Increasing the temperature to ~705 °C the La/MgO-MnNaWSi_0.1s catalyst is found to give ~6-fold higher or similar methane conversion compared to the MnNaWSi catalyst and La/MgO catalysts, respectively. However, the selectivity of the La/MgO-MnNaWSi_0.1s was 41%, which is higher by a factor of 1.5 for the La/MgO and 1.2 for the MnNaWSi, **Figure 1**. Interestingly, increasing the size of the La/MgO top-part of the bed showed diminished OCM performance, suggesting that the promoting catalytic effect is dictated by the lifetime of intermediate radicals. Data supporting our claim and relevant charechterization will be presented.

Figure 1. Temperature dependencies experiment (650-750 °C) for:

▬La/MgO-MnNaWSi_0.1s;

●La/MgO;

▲MnNaWSi



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Bifunctional catalysts for CO hydrogenation to fuels

V. Heczko[1], L. A. Silva,[2] R. M. B. Alves,[2] M. Schmal,[2] R. Giudici,[2] P. H. C. Camargo[1]

[1]*Department of Chemistry, University of Helsinki, Helsinki, Finland*
[2]*Department of Chemical Engineering, University of São Paulo, São Paulo, Brazil*
[*]*vilma.heczko@helsinki.fi*

Keywords: CO_2 to fuels, Fischer-Tropsch synthesis, iron-based nanocatalysts, zeolites

Introduction. Transportation, as well as other industries, is faced with a challenge of reducing the use of fossil fuels and lowering CO_2 emissions. Particularly challenging this is in aviation that contributes to 2-3 % of global CO_2 emissions. For this purpose, use of synthetic liquid fuels produced directly from CO_2 and H_2 is proposed. To advance this technology and improve the effectiveness from current processes, 4AirCRAFT project utilizes electro, chemo and biocatalysts combined in a single multistep catalytic reactor for production of sustainable aviation fuel.[1] Presented work focused on one of the steps of the process. It is based on the development of inorganic nanocatalysts and their performance evaluation for the CO hydrogenation to fuel-length hydrocarbons via Fischer-Tropsch process.

Experimental/methodology. We focused on bifunctional catalysts composed of iron oxide (Fe_3O_4) supported onto zeolite HZSM-5 (SiO_2/Al_2O_3=91) [2], denoted as Fe_3O_4/HZSM-5(91). The Fe_3O_4 nanoparticles were synthesized by precipitation and incorporated into HZSM-5 by two methods denoted as physical mixing and dry impregnation. For this, Fe_3O_4 was mixed with the zeolite in a mortar (dried, physical mixing) or in a form of a slurry (dry impregnation). We also tried a wet impregnation approach in which a solution of iron salt was impregnated on the zeolite followed by calcination. Catalytic tests were performed in an automated continuous fixed-bed reactor with control of gas flow, temperature, and pressure. Products were analyzed by gas chromatography. In addition, the effect of support acidity in CO conversion and product selectivity was evaluated, using zeolite materials with different SiO_2/Al_2O_3 ratios (from 52 to 371) generating the catalysts Fe_3O_4/HZSM-5(52), etc.

Results and discussion. Prepared Fe_3O_4/HZSM-5 catalysts were designed to target a tandem reaction of CO hydrogenation and chain growth on the Fe sites, and oligomerization/cracking secondary reactions on the acid sites of the zeolite support, leading to formation of longer-chain hydrocarbons. Our transmission electron microscopy data shows catalysts of Fe_3O_4 supported on HZSM-5 with morphologies consisting of clustered Fe_3O_4 nanoparticles deposited onto the zeolite. The XRD displayed diffraction peaks for the HZSM-5, Fe_3O_4 and α-Fe_2O_3 phases, whereas in wet impregnated catalyst, no iron species were detected. The catalyst prepared by dry impregnation showed smaller Fe crystallite size, compared to the physical mixing. The catalysts prepared by the different methods and different zeolite acidities were then tested in the Fischer-Tropsch reaction. The best results were obtained for the Fe_3O_4/HZSM-5(91) catalyst, with CO conversion of up to 89% at 350°C and lower CO_2 selectivity. Main products of the catalytic reactions were light hydrocarbons with approx. 25 % of liquid products in the gasoline range (C_4-C_8).

Overall, our data shows that the Fe_3O_4/HZSM-5(91) catalyst was active towards the hydrogenation of CO to hydrocarbons, and both the acidity of the zeolite and the synthesis method influenced the performances. A more detailed kinetic analysis as well as further optimization of the catalysts in terms of morphology and composition are under investigation to target higher-chain hydrocarbons and lower temperature conditions.

Acknowledgments
This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 101022633. This work is supported by Japan Science and Technology Agency (JST) under Grant Agreement No JPMJSC2102. This project is developed in the frame of a Mission Innovation Challenge. This work is also suppoted by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) under grants agreements No 2021/05329-7, 2022/07813-6, and 2022/04751-0.

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Aqueous-phase partial oxidation of methane with hydrogen peroxide over carbon-coated Fe-ZSM-5 catalysts

S. Hwang[1], M. Kwon[1], J Hwang[1,2*], ED Park[1,2*],

[1]*Department of Energy Systems Research. Ajou University, 206, World cup-ro, Yeongtong-gu, Suwon, Gyeonggi-do, Korea*
[2]*Department of Chemical Engineering, Ajou University, 206, World cup-ro, Yeongtong-gu, Suwon, Gyeonggi-do, Korea*
[*]*jongkook@ajou.ac.kr, edpark@ajou.ac.kr*

Keywords: Methane oxidation, ZSM-5, Carbon coating

Introduction. Methane, the simplest saturated hydrocarbon, is the main component of natural gas and shale gas. In spite of its abundance, it is currently used as fuel and its application as a chemical feedstock is rather limited. The current methane-based chemical process is based on an indirect pathway via syngas, a mixture of CO and H_2. Since this syn gas synthesis process is energy-intensive, only large-scale process is cost-competitive so that small-scale methane resource cannot be exploited. In order to overcome this weak point of an indirect methane conversion, the direct conversion of methane has been studied. Several methodologies are reported for the direct conversion of methane, including aromatization, coupling, pyrolysis, and partial oxidation of methane into oxygenates [1]. However, the strong C-H bond in methane makes it hard to convert methane directly into value-added products under mild condition [2]. In last decade, many researchers reported the selective oxidation of methane in an aqueous solution using H_2O_2 as an oxidant [3]. Xiao et al. proposed a "molecular fence" strategy that modifies the surface of the zeolite catalyst with hydrophobic organosilanes to control the diffusion of hydrophilic hydrogen peroxide and trap it inside [4]. In this study, the external surface of zeolite was modified with carbon originated from furfuryl alcohol (FA) and then a partial oxidation reaction of methane was performed.

Experimental/methodology. The experiment was performed in a glass liner inside an autoclave with a total volume of 120 mL. Hydrogen peroxide was added to water for its concentration to be 0.277 M. Methane was charged to the pressure of 31 bar. The product gas was separated with a Carbosphere packed column (Agilent) in an online gas chromatograph (Younglin), which was passed through a methanizer, methane from CO_2 was measured by a flame ionization detector. The liquid mixture was filtered with a microfilter (Millex) for nuclear magnetic resonance (NMR) analysis and hydrogen peroxide quantification. ^{1}H NMR was measured at room temperature via a Jeol Resonance ECZ600R, using 0.1 % trimethylsilylpropanoic acid (TMSP, Na salt)/D_2O (Euriso-top) as the standard.

Results and discussion. The physicochemical properties of the prepared catalysts were determined from N_2 physisorption data, NH_3-TPD, and contact angle measurement. As the content of carbon increased and then the external surface of zeolite decreased rapidly. The hydrophobicity of the surfaces was confirmed by water-droplet contact angle tests. When the carbon content is zero, the contact angle was 17.2 °. Also when the carbon content was 4.84 wt.%, the contact angle was 29.5 °. As the carbon content increases, the contact angle also increased, which means an increase in hydrophobicity. At 50 °C, H-ZSM-5 showed a total product yield of 401 μmol, C-H-ZSM-5 with a carbon content of 0.22 ~ 1.78 wt.% showed a total product yield of 500 μmol to 630 μmol. At 30 °C, 0.50 wt.% Fe-ZSM-5 showed a total product yield of 300 μmol, C-0.50 wt.% Fe-ZSM-5 with a carbon content of 0.27 ~ 3.41 wt.% showed a total product yield of 380 μmol to 650 μmol. The gain factor, which is defined as [moles of total products]/[moles of H_2O_2 consumed] for each catalyst was determined and was almost double over C-H-ZSM-5 than that over H-ZSM-5.

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Design of Nickel / Samarium Doped Ceria for Catalytic Partial Methane Oxidation

Andrew C. Chien[1,2*], Corinna C. Chi[1]

[1]*Department of Chemical Engineering, Feng Chia University, Taichung 40724, Taiwan*
[2]*Green Energy Development Center, Feng Chia University, Taichung 40724, Taiwan*
[*] *cyinchien@fcu.edu.tw*

Ceria has a wide range of applications on catalysis and energy categories. Inclusion of certain aliovalent dopants in the ceria can improve the catalytic performance by increasing the strain force of the latticeand generating more oxygen vacancies.We investigate the effect of synthesis parameters on the reaction activity, such as pH value, Sm/Ce ratio in SDC, and irradiation strength in a microwave synthesis. The result shows that the catalyst exhibiting high activities toward syngas production (i.e., a CH4 conversion > 90 % at 700 °C) requires a medium Ni-SDC interaction with a Sm/Ce ratio of about 1/9 to 2/8. As reported, optimum oxygen vacancies and adequate ion diffusivity in these SDCs, also displays the highest ion conductivity for fuel cell applications.

Keywords: Ceria, methane oxidation, oxygen vacancies, microwave synthesis, SDC

Introduction.

Partial oxidation of methane (POM) is an effective way for conversion of natural gas to valuable chemicals. Methane, a major component in natural gas, is partially oxidized in the POM to syngas with a suitable H2/CO ratio for methanol and Fischer–Tropsch synthesis. Compared with steam reforming of methane, the POM is mildly exothermic, thus avoiding highly endothermic reaction with a smaller reactor size and reduced capital cost [1]. Besides, a higher efficiency can be achieved when the POM is combined with a membrane reactor to produce hydrogen for electric power generation [2].

Several studies have focused on metal oxides such as doped ceria (Ce) for conversion of methane . Ceria, an excellent electronic and ionic conductor, has been shown to be an effective catalyst for methane oxidation because of high resistance to sintering and coking. In addition, ceria doped with trivalent cation such as samarium (Sm) exhibits mixed-valence states of Ce4+ /Ce3+ as a redox couple in the POM. Accordingly, doped ceria may play a synergistic role and provide additional pathways for redox reaction to improve the POM activity [3].Many preparation methods have been applied to prepare a metal/doped ceria system for catalytic applications, such as microwave, hydrothermal, co-precipitation, sol–gel techniques and so on [4]. Several nickel/ samarium doped ceria (Ni/SDC) systems prepared by a microwave method are shown to exhibit smaller crystallites with high activity in comparison with those in the conventional process. In the present study, we obtained SDC nanopowders via a microwave method and made Ni/SDC catalysts by combination of SDC with nickel via different routes. The effect of preparation methods and synthesis parameters on the POM activity was investigated. Our results showed that different methods and parameters lead to changes in morphology and particle size, which are crucial for the catalytic activity.

Experimental/methodology

Catalyst preparation

The synthesis of samarium doped cerium oxide (SDC) was achieved by a microwave (MW) assisted method in a two-step process of, (i) MW irradiation of precursor solution, and (ii) crystallization of the fluorite structure by heat treatment [5]. In a typical preparation, cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) and samarium(III) nitrate hexahydrate ($Sm(NO_3)_3{\cdot}6H_2O$) as precursor salts were dissolved in ethanol with Sm/Ce molar ratio according to a composition of $Ce_{0.1}Sm_{0.9}O_{1.95}$. The mixture was dropwise added with 10 M NaOH for adjustment of pH value and then placed inside a conventional household

microwave. The synthesis was conducted by irradiating the solution with different microwave strength (Low = 133W、Med = 532W、High = 798W) in an on/ off cycle (10 sec on and 20 sec off) for 10 min. The precipitate from the irradiated solution was collected and washed with distilled water to remove soluble species. The sample was further rinsed with ethanol and then calcined at 600 ℃ for 4 h to yield the product (SDC).

Characterization

Catalytic activity on methane oxidation was evaluated by temperature-programmed reaction with an on-line mass spectrometer. Mass/electron ratio (m/e) in the MS were selected for H_2 (2), He (4), CH_4 (15), H_2O (18), CO (28), O_2 (32), and CO_2 (44). The phase composition of crystalline components on the catalyst was investigated by X-ray diffraction (XRD) analyses. The assignment of the various crystalline phases was based on the JPDS powder diffraction file cards. The morphology of the as-synthesized Ni/SDC catalyst was characterized by scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDX) and transmission electron microscope (TEM).

Results and discussion.

Figure 1 shows X-ray diffraction (XRD) patterns of the as-synthesized catalyst. The XRD pattern of SDC on all catalysts was found to match well with the cerium oxide and indexed to a cubic fluorite structure. There were no peaks detected for the dopant samarium oxide, indicating that the dopant ion is fully substituted in the CeO_2 lattice to form a solid solution. Figure 2 presents MS profiles of eluting gaseous products from methane oxidation on the CMW catalyst prepared at different pH values. The result of temperature-programmed surface reaction shows that syngas are main products. The catalyst prepared at a low pH value produced more syngas with a higher MS intensity, whereas the catalyst prepared at a high pH value gave rise to a more stable activity. CMW catalysts yield syngas in methane oxidation and the highest activity is achieved on the lowest pH made catalyst, i.e., pH = 9.

Figure 1 XRD patterns of the synthesized Ni/SDC catalyst

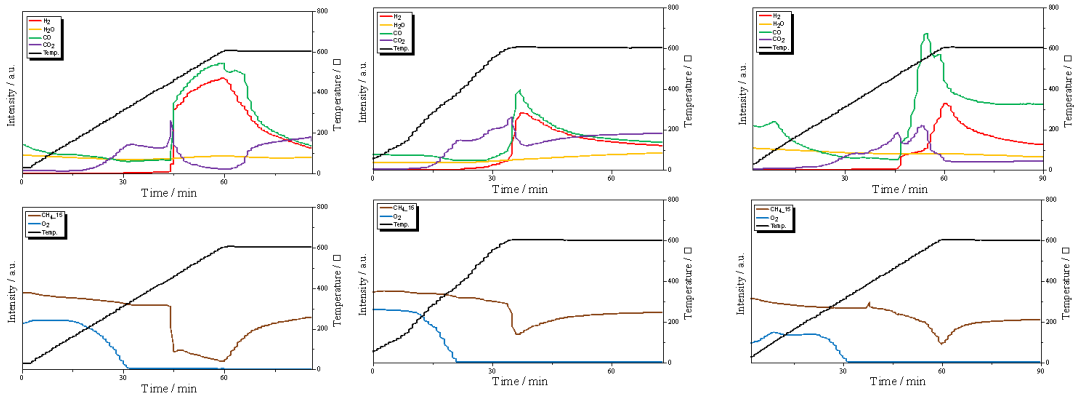

Figure 2 MS profiles of eluting gas products from methane oxidation at 700 °C on the Ni/SDC catalyst prepared at different pH values

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Aqueous-phase partial oxidation of methane over Fe-ZSM-5 with in situ generated H_2O_2 over Pd/C

J. Kang[1], E. D. Park[1,2,*]

[1]*Department of Energy Systems Research, Ajou University, Suwon, Republic of Korea*
[2]*Department of Chemical Engineering, Ajou University, Suwon, Republic of Korea*
[*]*edpark@ajou.ac.kr*

Keywords: Partial oxidation of methane, In situ H_2O_2, Methanol, Formic acid

Introduction. The direct conversion of methane to its oxygenates is known as one of challenging reactions. The current methane conversion into the value-added products is based on the indirect energy-intensive multistep processes in which methane is first converted into a syngas, a mixture of carbon monoxide and hydrogen, at high temperatures. Therefore, this indirect process can be industralized in a large scale to get its economic competitiveness. In order to utilize small-scale methane resources, it is important to develop efficient direct methane conversion technologies including direct partial oxidation, dimerization, and chlorination at low temperatures[1]. However, the chemical inertness of methane and its more stable C-H bond than that of its oxygenates make it difficult to obtain high yields of desired products during direct methane conversion[2]. Hutchings et al. reported the partial oxidation of methane over Fe/ZSM-5 catalysts using H_2O_2 as an oxidant[3]. In our previous work, we reported the partial oxidation of methane over Fe/ZSM-5 and Pd/C catalysts. Pd/C catalyst was used for the synthesis of H_2O_2 in situ from H_2 and air(O_2)[4]. The pH of the reaction liquid was adjusted using sulfuric acid to obtain a higher H_2O_2 concentration despite of leaching of the active metal. In this work, we conducted partial oxidation of methane using air, which is more economic than H_2O_2, as an oxidant and H_2 as a reducing agent. The H_2O_2 was synthesized in situ from the air(O_2) and H_2 and utilized for the conversion of methane. The commercial Pd on activated carbon was used for H_2O_2 synthesis and Fe/ZSM-5 was used for the partial oxidation of methane. To increase the yield of H_2O_2, various halide anions including KF, KBr, and KCl were used without any liquid acids. The effect of some reaction variables such as reaction temperature, reaction time, and the concentration of halide anions on the catalytic performance was also investigated.

Experimental/methodology. The Fe/ZSM-5 catalyst was prepared with a wet impregnation method using $FeCl_3$ as a Fe precursor and NH_4-ZSM-5 as a support. 1%Pd/C catalyst was purchased from Sigma Aldrich and used as-received. The liquid-phase partial oxidation of methane was conducted in an autoclave. Typically, 50 mg of Fe/ZSM-5, and 50 mg of 1 wt.% Pd/C were added into 30 mL of water including halide anions with various concentrations(0-10 mM). The reactor was sealed and reactant gases were charged (CH_4:H_2:Air=15:3:10 bar).

Results and discussion. The yield of methane oxygenates and H_2O_2 was the highest when KBr was used as an additive. As the concentration of KBr increased, the amount of total product and H_2O_2 after the reaction increased. However, the use of KBr at high concentrations caused the leaching of active metals from the catalysts, even though the fraction of leached metal didn't exceed 0.5% of the introduced amount. When the reaction time was increased from 30 min to 2 h, the amount of total products increased gradually but the residual H_2O_2 and methane oxygenates selectivity decreased. Increasing reaction temperature from 30 to 50 ^{o}C resulted in higher methane oxygenate yield but lower methane oxygenates selectivity. Under optimal reaction conditions, the conversion of methane reached 0.4 % with methane oxygenates selectivity of 88 %(reaction time= 4h, temperature= 30 ^{o}C, [KBr]= 10 mM).

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Determining bifunctionality of mesoporous Co/Zeolite catalyst for direct synthesis of liquid fuel by Fischer-Tropsch reaction

Sungtak Kim[1*]

[1]*Department of Chemical Engineering and Applied Chemistry, Chungnam National University, Daejeon, South Korea*

Keywords: Fischer-Tropsch, Cobalt catalyst, Mesopore Zelite

Introduction.
Fischer-Tropsch (FT) synthesis from natural gas is one of the most promising technology for the production of clean fuel that is served as an alternative of traditional petroleum oil. In general, additional upgrading process such as mild hydrocracking or isomerization is accompanied for the production of liquid fuel from solid wax. To simplify the processes, dual-function catalysts that exhibited activities for both chain growth and isomerization reaction have been suggested for the single FT process. For this purpose, a ZSM-5 zeolite was proposed as a support material due to its wide presence of acid site that is capable of cracking and isomerization of long-chain hydrocarbons. Utilization of mesoporous ZSM-5 is one of the most potential solution for the above issue.1 However, microscopicrole of mesoporosity on the activity and selectivity of the Co/ZSM-5 catalyst for the FT reaction are still elusive. Therefore, in this work, the effects of mesoporosity and acidity of Co/zeolite catalysts on the activity and selectivity for the FT synthesis were systemically studied.

Experimental/methodology.
Mesoporosity was implemented to HZSM-5 by two different methods, so-called the bottom-up and top-down methods. The bottom-up method refers to providing mesopores by controlling the degree of crystallization during when hydrothermal synthesis ofsynthesizing HZSM-5 crystal. For instance, HZSM-5 synthesized at 120 °C exhibited a low degree of crystallinity accompanying mesopores with 22 nm of pore size, while that synthesized at 160 °C exhibited a high degree of crystallinity without mesopores. In the present study, the low crystalline mesoporous HZSM-5 and the high crystalline HZSM-5 are denoted as bm-HZSM5 and b-HZSM-5, respectively. The top-down method refers to the alkali treatment that randomly de-silicatesetches the parent HZSM-5 structurecrystal, resulting in a creation of mesopores.

Results and discussion.
Mesoporous Co/HZSM-5 exhibited higher activity than conventional-structure Co/HZSM-5 and produced liquid form hydrocarbons. The mesoporous ZSM-5 zeolite was accompanied with large external surface area, which led to an effective Co dispersion. Since the FT synthesis conducted in the present study was not a case of diffusion-limited reaction, the mass-transfer enhancement induced by the mesoporosity was not responsible for its high activity. Cracking and isomerization abilities were linearly correlated to the number of acid site present on the zeolite support but independent to its mesoporosity.

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Direct CO_2 Hydrogenation via Fischer-Tropsch Synthesis over Cobalt Catalyst Supported on La-doped Cerium Oxide

H. Konno[1], S. Harada[2], A. Yanagita[1], K. Tashiro[1,3], M. Ogura[2], S. Satokawa[1,3*]

[1] *Graduate School of Science and Technology, Seikei University, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo 180-8633, Japan*

[2] *Instutute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro, Tokyo 153-8505, Japan*

[3] *Faculty of Science and Technology, Seikei University, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo 180-8633, Japan*

[*] *satokawa@st.seikei.ac.jp*

Keywords: Direct CO_2 conversion, Fischer-Tropsch synthesis, cobalt catalyst, La-doped ceria, oxygen vacancy

Introduction

The conversion of CO_2 to liquid fuels via catalytic reactions has attracted great attention to the realization of a carbon-neutrality. Regarding this, two subsequent catalytic reactions: the reverse water gas shift (RWGS) reaction followed by Fischer-Tropsch synthesis (FTS) is a promising strategy. The former reaction produces CO from CO_2, and the latter affords hydrocarbons from CO. Our next stage is the development of a highly active catalyst for one step conversion of CO_2 (CO_2-FTS) to simplify the process design.[1] In general, cerium oxide (CeO_2) can generate oxygen vacancies which act as CO_2 adsorption sites by doping trivalent cations such as La^{3+}.[2] We synthesized cobalt catalysts, promoting alkyl-chain growth, on La-doped CeO_2 (LC) with the expectation that LC and cobalt become the reaction fields for the RWGS and the FTS, respectively.

Experimental/methodology

Lanthanum (III) nitrate hexahydrate and cerium (III) nitrate hexahydrate were dissolved in deionized water. The solution was dropped into a continuously stirred 10% NH_3 solution and kept stirring at room temperature for 24 h. The resulting precipitate was collected by filtration and then dried at 110°C overnight. The obtained powder was calcined at 400°C for 5 h. The material in which *x* mol% of Ce^{4+} is replaced by La^{3+} is denoted as LCx. The cobalt was loaded on LCx by impregnating to prepare catalysts (Co/LCx), and then calcined at 400°C for 6 h. The obtained Co/LCx catalysts were reduced with H_2 at 400°C for 2 h and catalytic activity was evaluated at 1.0 MPa, H_2/CO_2 = 3, 260–300°C. The outlet gas was analyzed using a gas chromatograph.

Results and discussion

Fig. 1 shows the CO_2 conversion and the selectivity of products on CO_2-FTS at 260°C. Although, the CO_2 conversion was decreased gradually as the molar fraction of La^{3+} increased in the support, the "C_{5+}, Others" selectivity was increased accompanied with a decreasing in "CH_4" selectivity. The surface oxygen vacancies in the obtained LCx were analyzed by XPS spectra of O 1s orbitals. The peaks derived from O 1s can be resolved into oxygen atoms in the CeO_2 lattice (O_L) and hydroxyl groups adsorbed in oxygen vacancies on the surface (O_V).[3] The area ratio O_V/O_L of these peaks became larger as the amount of the doped La^{3+} increased, indicating that La^{3+}-doping formed oxygen vacancies. These results demonstrate that the formation of oxygen vacancies in CeO_2 by La^{3+}-doping is a promising strategy for the execution of CO_2-FTS in one step.

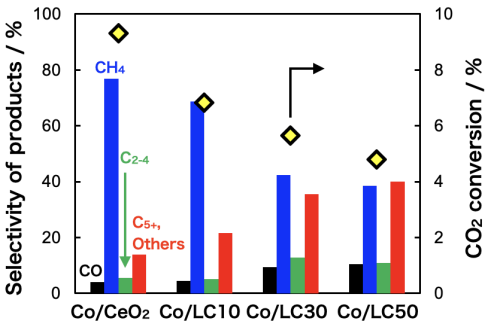

Fig. 1 CO_2 conversion and selectivity of products on the CO_2-FTS at 260°C. C_n and Others imply hydrocarbon with carbon numbers of *n*, and products except for hydrocarbons

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Optimization of dual-bed catalyst system for linear alpha olefin production in alcohol dehydration

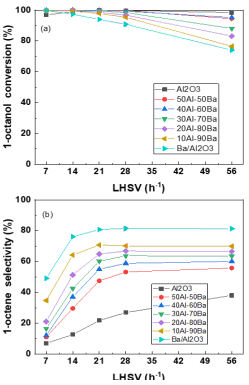
Y. Kim[1,2], U. Jung[1], D. H. Chun[1], M. H. Youn[1], K. B. Lee[2], K. Y. Koo[1*]

[1]*Korea Institution of Energy Research, Daejeon, Korea*
[2]*Korea University, Seoul, Korea*
[*]*kykoo@kier.re.kr*

Keywords: linear alpha olefin, alcohol dehydration, dual-bed system

Introduction. Linear alpha olefins (LAOs) are olefins with a double bond at the end of the linear carbon chain. They are used as raw materials in the chemical industry as a co-monomer of polyolefins, synthetic luricants, plasticizer alcohols, and surfactants. The demand for C4-C8 LAO accounts for more than half of the total LAO demand. Hence, alcohol dehydration has recived increased attention owing to its high selectivity of specific LAOs which are used for LLDPE co-monomers. Generally, weak acidic metal oxide catalysts are utilized in alcohol dehydration reactions because their acidic sites serve as active sites. As the acidity of the catalyst increases, the concentration of active sites on the catalyst surface also increases, resulting in increased 1-alcohol conversion. However, side reactions (dehydration-hydration-dehydration) entail the formation of double-bonded isomers, which cause problems in the downstream separation process [1]. Both alcohol dehydration and isomerization can occur at the acidic sites of the catalyst; hence, there exists a trade-off between 1-alcohol conversion and LAO selectivity, and this correlation surpresses the LAO yield. In this study, we applied Al_2O_3 catalysts (Al) with high acidity and Ba/Al_2O_3 catalysts (Ba) with high LAO selectivity in a dual-bed system and investigated the optimum Al-Ba bed ratio for catalytic performance in the 1-octanol dehydration reaction.

Experimental. The commercial Al_2O_3 sphere (Sasol, 1 mm) precalcined at 500 °C was used as the catalyst. The 1.5 wt% Ba/Al_2O_3(Ba) was prepared using the incipient wetness method. The chracteristics of the catalysts were investigated by ICP-MS, XRD, BET, CO_2-TPD, and pyridine-FTIR. The catalyst test was performed at 400 °C with LHSV 7 – 56 h^{-1}. The hydrocarbon products were quantitatively analyzed using a GC-FID (Agilent 7890 B equipped with an HP-5 column). The stability test was conducted at 400 °C with LHSV 21 h^{-1} for 100 h.



Results and discussion. Various dual-bed systems (Al-Ba, Al+Ba (physical mixing), and Ba-Al) were examined for 1-octanol dehydration(not shown here). Among these, the Al-Ba system with Ba/Al_2O_3 positioned at the end of the catalyst bed exhibits the highest 1-octene purity [2]. The effect of the Al-Ba bed ratio on the activity of the Al-Ba catalyst system was investigated (Fig. 1). The Al-bed ratio affected 1-octanol conversion because the Al_2O_3 ratio incresed the concentration of acid sites in catalyst bed. Interestingly, 1-octene selectivity increased in propotion to Ba-bed ratio. Furthermore, the basicity of the catalyst hindered the side reaction by readsorption of 1-octene and supressed the formation of octenes isomer. Notably, the optimal Al-Ba ratio varied depending on the flow rate. The 10Al-90Ba system with a high Ba-bed ratio exhibited a high 1-octene yield (34.7 %) under high conversion at LHSV 7 h^{-1}. Meanwhile, at LHSV 56 h^{-1}, the 60Al-40Ba system showed the highest 1-octene yield (57.3 %). Based on these results, stability tests were conducted on the dual-bed (10Al-90Ba, 40Al-60Ba) and single-bed systems (Al_2O_3, Ba/Al_2O_3). Minimal changes were observed in the 1-octanol conversions of all the catalyst systems with respect to time on stream (not shown here). Notably, the dual-bed system maintained high durability compared to the Ba single-bed system. Moreover, the 10Al-90Ba system exhibited excellent stability and high 1-octene yield, making it the most efficient catalyst for alcohol dehydration and 1-octene production.

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Pre-Carburization Effect in Hybrid Catalytic System: Optimistic Process Development for Gas to Liquid Fuel Production

M. S. Kutubi[1*], K. Sato[1], Y. Shimura[2], S. Inagaki[2], Y. Kubota[2] and K. Nagaoka[1*]

[1]*The Graduate School of Engineering, Nagoya University, Nagoya, Aichi 464-8603, Japan*
[2]*Graduate School of Engineering Science, Yokohama National University, Yokohama 240-8501, Japan*
[*]*kutubi.shahajahan@material.nagoya-u.ac.jp*, [*]*nagaoka.katsutoshi@material.nagoya-u.ac.jp*

Keywords: Pre-carburization, Hybrid catalyst, Green Liquid Fuel.

Introduction: The global issues: global warming and a shortage of fossil fuels: gas, oil *etc.* making an uncertainty in sustainable development goal resulting the price-up of commodity: energy, fuels, foods *etc.* has called for the synthesis of green liquid fuels (GLF): gasoline, diesel and jet-fuel. CO hydrogenation called Fischer-Tropsch (FT) process is well known for efficient GLF production by using syngas synthesized from H_2O and CO_2 accused for global-warming, but proficient process is still limited for low yield. On GLF production, many articles emphasized the Co/Al_2O_3-based systems in industrial application uniquely for low-price/stability of Co and Al_2O_3[1] focusing the role of Co-surface modification in change of acidity-basicity, reducibility, dispersion *etc.* by extra addition of inorganic oxides or organic moieties (OM) to increase activity with higher yield.[2,3,4] OM effect in surface modification of hybrid/nonhybrid Co-based catalyst for FT is still very limited, although their positive effects enhance the catalytic efficiency. Therefore, based on aiming to develop a proficient FT process for GLF production, our finding pointed out the OM effect in Co-based hybrid catalyst, and revealed very high stability and efficiency in gas to GLF production.

Experimental: Co/Al_2O_3 using Co-organic precursor was prepared in usual wet-impregnation method and finally, it was hybridized with zeolite, marked as xCo(O)-**Hcat** (x = wt%). For GLF synthesis, its activity after in-situ reduction was evaluated in a fixed-bed FT process at H_2:CO/2:1 in 13-26 (g_{cat}·h)/mol, 1.0 MPa, and 210-230°C and all species was quantified in online GC (TCD/FID), and offline GC-MS and offline FID-GC.

Results and discussion. At first, 20-40Co(O)-**Hcat** at the above FT conditions were tested and the results showed excellent stability with high activity, high yield (>65%) and selectivity (72-84%) to GLF: C_5-C_{19} exploring significant decrease of CH_4 and CO_2 for 30Co(O)-**Hcat** compared to those for 20Co(O)-**Hcat** and 40Co(O)-**Hcat**, but OM free 30Co(N)-**Hcat** ($Co(NO_3)_2$ precursor used) resulted in low efficacy to GLF shown in Fig. 1. Furthermore, Co/Al_2O_3 hybridization enhanced the selectivity to gasoline-range GLF (C_5-C_{11} in >70%) with suppressing CH_4 and CO_2 relative to those for nonhybrid Co/Al_2O_3. Here the study of HRTEM, H_2-TPR and TG confirmed the C-existence in **Co(O)-Hcat**, while the HRTEM disclosed C-coated cobalt species (**A**). Despite the higher **A** formed with the higher Co loading, 30Co(A)-**Hcat** afforded higher efficacy for a proper combination developed between **A** and zeolite. Besides, a long-time heat treatment of 30Co(O)-**Hcat** resulted in decarburized 30Co(12h)-**Hcat** that showed a notable drop of efficiency to GLF by CO_2 and CH_4 increase due to the active surface-structure change for absence of C-species. Here, we assume that such combination developed the active $Co^{\partial+}$—$C^{\partial-}$ phase and textural properties, which enhanced the chain-propagation for modification in CO and H_2 activation[4] without C-deposition, affording the higher efficiency and selectivity to GLF, while C-deposition was confirmed for Co(N)-**Hcat** and Co(12h)-**Hcat** for the FT stability. More investigation is still now progressing, and we think it would be open a new door to design the hybrid catalysts for CO/CO_2-hydrogenation in the future.

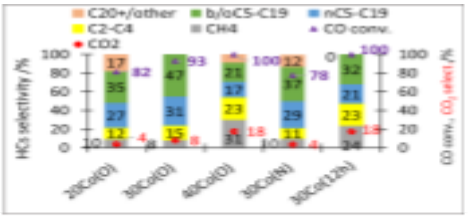

Fig. 1. Pre-carburized Co-**Hcat** Effect in HCs (hydrocarbons) distribution with FT efficiency. efficacy.

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Catalysts of Zr-based metal-organic framework applied in the direct oxidation of methane to methanol

Thielle N. V. S. Ferreira[1], Janaina F. Gomes[1] and Jose M. Assaf[1]
[1]*Federal University of São Carlos, São Carlos, Brazil*
[*] *janainafg@ufscar.br*

Keywords: methane, methanol, metal organic framework, MOF-808.

Introduction

The direct conversion of methane into methanol is an important challenge to be overcome due to the strong C-H bond, high ionization energy of methane and excessive oxidation of methanol [1]. In the literature, metal organic frameworks (MOFs) present attractive characteristics for their application as catalysts and some of these structures have shown to be promising for the conversion of methane to methanol, especially those containing copper [2]. This work aims to study Cu-MOFs with varying Cu loading applied in the direct oxidation of methane to methanol at low temperature and atmospheric pressure, as well as the reuse of these materials. MOF-808, which is a Zr-based MOF, was synthesized using the solvothermal method. Subsequently, a post-synthesis step was performed to add an organic ligand, namely EDTA, and incorporate Cu II. The catalysts were characterized by X-ray fluorescence, X-ray diffraction and thermal analysis. The catalytic activity of Cu-MOF-808 was evaluated.

Experimental/methodology

MOF-808 and MOF-808-EDTA were synthesized following the procedure previously reported in the literature [2]. Copper incorporation was carried out with nominal Cu/Zr molar ratio of 1.8, 1.9, 2.0, 2.1. Catalytic experiments were carried out in three steps: (1) catalyst activation with oxygen at 150 °C, (2) methane oxidation at 150 °C and (3) product extraction in water.

Results and discussion

The diffractograms of the investigated samples presented in Figure 1a are in agreement with the simulated MOF-808, showing that the metallic organic structures were successfully synthesized [1]. From Figure 1b, three regions of loss of mass can be observed. Up to 100°C the loss of mass is associated with samples humidity, up to 250°C physically adsorbed trimesic acid (BTC) is released and, from 250°C onwards the loss of mass is related to the removal of modulator and solvent [3]. As shown in Figure 1c, the average methanol productivity ranged from 54 to 90 µmol g^{-1}cat, being higher for the MOF-EDTA-1.9Cu and MOF-EDTA-2.0Cu catalysts, indicating an effect of copper loading on the production of methanol. Results of the catalyst reuse (Figure 1d) show a decrease of the methanol productivity with increasing number of reuse cycles, although it is less pronounced from the 2nd to the 3rd cycle. The impact of the Cu loading on the methanol productivity and the cause of the samples deactivation are being further investigated.

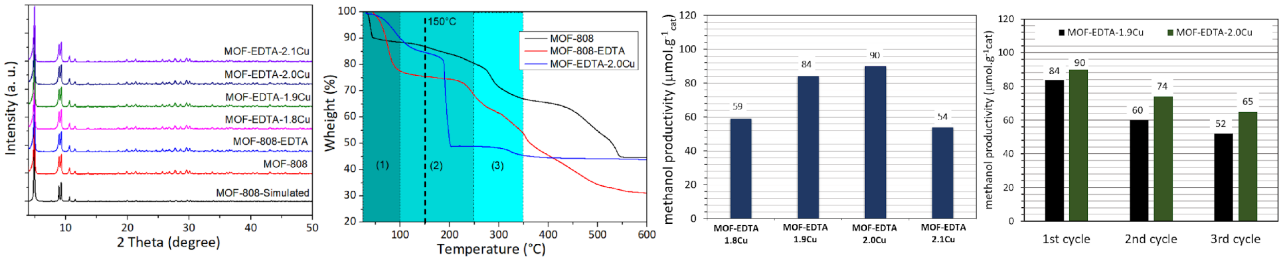

Figure 1. a) X-ray diffractograms of MOF-808 and post-synthesis modified materials, b) thermogravimetric analysis of MOF-808, MOF-808-EDTA, MOF-EDTA-2.0Cu samples, c) methanol productivity and d) reuse evaluation of MOF-EDTA-1.9Cu and MOF-EDTA-2.0Cu catalysts.

Acknowledgments

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Measurements of spatially-resolved concentration profiles on Fischer-Tropsch synthesis in a fixed-bed compact profile reactor

J. Mettke[1*], F. Wolke[1], S. Hilbig[1], E. Reichelt[1], M. Jahn[1]

[1]*Fraunhofer IKTS, Dresden, Germany*
[*]*judith.mettke@ikts.fraunhofer.de*

Keywords: Fischer-Tropsch synthesis, Reaction profiles, In-situ analysis

Introduction. Fischer-Tropsch synthesis (FTS) has recently experienced renewed interest, as hydrocarbon chains can be built up from hydrogen and carbon monoxide (syngas) via a heterogeneously catalysed chain growth reaction [1]. Therefore, FTS plays a major role in power-to-X concepts and is considered one of the key technologies for the energy transition process. Since syngas cannot only be obtained from fossil but also from renewable carbon feedstocks such as biogas and CO_2 [2], the sustainability of the production of fuels or other valuable products like higher alcohols can be notably increased using FTS. The Fischer-Tropsch synthesis is characterized by a large reaction network and a product mixture of hydrocarbons from different substance groups and chain lengths. The product spectrum is also strongly dependent on the reaction conditions. Although the first insights into this reaction were published in the 1920s [3], the underlying reaction mechanisms and kinetics are still poorly understood due to their complexity. This leads to difficulties in process optimization according to ecological and economic criteria.

Experimental/methodology. Conventional slurry or fixed-bed reactors allow only integral measurements of product selectivity and derived parameters like chain growth probabilities [4]. Hence innovative reactor designs are required to gain more insights than classical integral reactor setups. The application of the so-called compact profile reactor (CPR), developed by *Reacnostics GmbH* (Hamburg, Germany), can give access to previously inaccessible information. This setup allows for the local sampling of the gas phase at distinct positions in the catalyst bed so that using gas chromatographic methods spatially resolved profiles of the individual product species can be obtained [5]. Thus, the CPR offers the possibility to derive differential data within fixed beds at reaction conditions.

Results and discussion. In the first experiments on FTS on iron-based catalysts, spatially resolved concentration profiles could be obtained for short-chain components, leading to promising new insights into the influence of operating conditions as well as of secondary reactions on product selectivity [6]. To also obtain spatially resolved concentration profile data of long-chain hydrocarbons and to determine meaningful reaction kinetics, it is necessary to improve the existing experimental setup. For this purpose, advanced on-line analysis and the possibility of dosing both liquids and gases will be used, which will enable co-feed experiments. The current state of development and future improvement of spatially resolved profile measurements for Fischer-Tropsch synthesis will be presented.

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The conversion of methane to methanol with in situ generated H_2O_2

Fenglou Ni[1], Richard J. Lewis[1], Graham J. Hutchings [1*]

[1]*Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK.*
[*]*E-mail: hutch@cardiff.ac.uk*

Keywords: Methane oxidation, H_2O_2, Methanol

Introduction.
As methane is the most abundant component in natural gas, it remains a great challenge to directly convert methane to valuable chemicals with both high activity and high selectivity under mild conditions.[1,2] Currently, hydrogen peroxide (H_2O_2)[3] and nitrous oxide[4], as the oxidants, are often used to directly activate methane. But both oxidants would limit the industrial application due to the high cost or environmental-related problems. Instead of using the above oxidants, researchers also used molecular oxygen (O_2) to promote the selective oxidation of methane to oxygenates.

To date, Pd-based catalysts are efficient for the direct synthesis of H_2O_2 from O_2 and hydrogen (H_2), which can further decompose into the active hydroperoxyl and hydroxyl species to oxidize methane.[5] However, due to the low activity of oxygen and the overoxidation of the oxygenates, the methane oxidation reaction with O_2 or O_2/H_2 suffers from low activity and poor oxygenates selectivity. Here, we synthesized zeolite-supported AuPd catalysts to activate methane with in situ formed H_2O_2 from H_2 and O_2.

Experimental/methodology.
The oxidation of methane was carried out using a Parr stainless steel autoclave with a nominal volume of 50 mL reactor and a maximum working pressure of 2000 psi. To evaluate catalytic activity towards the autoclave was charged with catalyst (0.027 g) and solvent (10 g H_2O, Fischer Scientific, HPLC grade). The reactor was purged with methane (100 psi) and then charged with pure H_2, N_2, O_2 and CH_4 such that the total pressure equalled 435 psi. The gas phase composition was 0.8% H_2/ 1.6% O_2/ 76.7% CH_4/ 20.8% N_2 to ensure the mixture was outside of the explosive limits. The autoclave was then heated to the desired reaction temperature (50 °C), once at the set temperature, the reaction solution was stirred at 1500 rpm for 0.5 h.

Results and discussion.
We prepared a series of AuPd catalysts with different ratios for the in situ methane oxidation. with the Au:Pd ratio approaching 1:1, the catalyst showed the highest methanol productivity and H_2O_2 productivity. Although the Pd-only catalyst showed greater H_2O_2 productivity, no methanol was observed during the reaction. Thus, the addition of Au could not only improve the formation of H_2O_2, but also favor the activation of methane. Such trends may indicate the key role of alternative reactive oxygen species (•OOH, •OH and $•O_2^-$) for methane oxidation which has been reported previously. Moreover, optimizing the total loading of Au and Pd and the preparation methods might further improve the performance.

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Heat transfer intensification in tubular reactors for the Fischer-Tropsch synthesis by adopting conductive cellular internals: a pilot-scale study

Martino Panzeri[1], Carlo Giorgio Visconti[1], Gianpiero Groppi[1] and Enrico Tronconi[1]*

[1]*Laboratory of Catalysis and Catalytic Processes, Politecnico di Milano, Milan (Italy)*

[*]*enrico.tronconi@polimi.it*

Introduction. The interest in the application of highly conductive internals for the intensification of processes controlled by heat-management has grown significantly [1]. Such an option becomes even more interesting if the catalyst is packed inside the cellular structure, rather than dispersing it by washcoating. We report the application of this concept to the Fischer-Tropsch synthesis (FTs) in a pilot-scale reactor. The choice of the FTs as a demo reaction originates from the high current industrial interest, but also from its high reaction enthalpy ($\Delta H°_r$=-165 kJ/mol) and high temperature sensitivity, which make this process the perfect case study to explore the impact of shifting from convective (packed beds) to conductive heat transfer. The experimental activity has been focused on the selection of geometry and design of the conductive cellular reactor internals for the maximization of the heat transfer rate. Different reactor configuration were tested and, adopting the packed bed as reference, we show the advantages of introducing conductive internals. Aluminium open cell foams (OCF) [2] and periodic open cellular structures (POCS) [3] with skin are the internals herein tested.

Materials and methods. Experiments were carried out on a semi-pilot FTs rig. The Co/Al_2O_3 catalyst particles (dp=300 μm) were packed inside an externally cooled, jacketed tubular reactor, 1 m long and 28.80 mm I.D.. The catalytic bed (20 cm in depth) was positioned at the central zone of the tube, in which one single internal (L = 20 cm), or two (L = 10 cm each) were introduced. The cooling fluid was diathermic oil flowing with high rates. The FTs tests were carried out at 25 barg, with a GHSV of 4 Nl/h/g_{cat}, feeding syngas with a H_2/CO ratio of 2.1. The thermal behavior of the structured reactor was studied at different heat duties, varying the coolant temperature and measuring the axial temperature profiles along the reactor centerline (T_c), as well as the skin temperature of the reactor (T_w).

Results and discussion. The introduction of highly conductive internals (Al OCF and POCS) (Figure 1) enabled up to 70% CO conversion per pass. For each tested configuration, an overall heat transfer coefficient was estimated from the slope of the linear fit of the data (Figure 1, left), where Q_{sup} is the reaction heat divided by the heat exchange surface, $T_{c,avg}$ is the average catalyst temperature at the centerline and $T_{w,avg}$ is the average temperature of the reactor wall, confirming the advantages of OCF and POCS application. The adoption of Al open cell foams (dc= 2 mm, void fraction ε=0.88) incremented the heat transfer coefficient by one order of magnitude (400 W/m^2/K), allowing to operate at temperatures and CO conversions which are not accessible by the packed bed reactor (40 W/m2/K). An even better result was achieved when testing an engineered structure: POCS with skin (dc=3 mm, void fraction ε=0.80). For this kind of internals, the research was focused also on the benefits offered by the improved contact of the structure with the reactor wall, studying the effect of varying the "gap" (POCS – tube clearance) on the heat transfer performance. The last experiments involved the adoption of POCS with the skin (dc=3 mm, ε=0.69). The new internal design enabled CO conversions above 70% with an overall heat transfer coefficient exceeding the outstanding value of 1200 W/m^2/K.

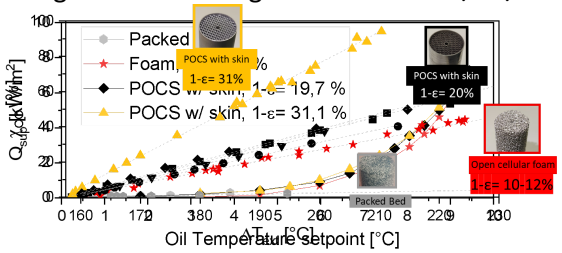

Figure 1. (left) Specific heat duty vs. ΔT_{ext} (= $T_{c,avg}$ - $T_{w,avg}$). (right) CO conversion vs. oil temperature setpoint.

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Selective Production of Hydrocarbon via Fischer-Tropsch Synthesis Using Bifunctional Iron-Zeolite Catalysts

G. B. Rhim[1], K. Y. Kim[1], M. H. Youn[1], D. H. Chun[1,*]

[1]Carbon Conversion Research *Laboratory, Korea Institute of Energy Research, Daejeon, Republic of Korea*
[*]*cdhsl@kier.re.kr*

Keywords: Fischer-Tropsch synthesis, Bifunctional catalysts, Iron-based catalysts, Zeolites

Introduction.

Low-temperature Fischer-Tropsch synthesis (LT-FTS) is an attractive way to produce liquid fuels from syngas (CO + H_2). LT-FTS is considered a preferred method for selectively producing liquid fuels due to its ability to minimize gaseous hydrcarbon (C_1-C_4) generation [1]. The wide distribution of C_{5+} hydrocarbons in LT-FTS can be the main drawback when used as liquid fuel, which requires an additional hydrocracking process to convert FTS waxes into liquid hydrocarbon range (C_5-C_{20}) [2]. The bifunctional catalysts consisting of iron-based catalysts and zeolites can be used to improve the selectivity and yield of liquid hydrocarbons in LT-FTS without required for additional hydrocracking processes. The acid sites of zeolites in bifunctional catalysts usually dictate the selectivity of the desired products. Therefore, it is essential to understand the precise relationship between acidity and hydrocarbon distribution in order to precisely design bifunctional catalysts. However, no study has reported a clear correlation between acidity and the distribution of hydrocarbons. In this study, we report a linear correlation between the acid sites and the cracking rate in the bifunctional process of LT-FTS and cracking for the first time, in which bifunctional catalysts were physically mixed with the precipitated iron-based catalysts and H-ZSM-5.

Experimental/methodology.

The bifunctional model catalysts by physically mixing industrially important precipitated iron-based LT-FTS catalysts and H-ZSM-5 to exclude any undesired chemical interactions between the two catalysts. The acidity of the model catalysts was controlled by adjusting the ratio Si/Al and the ratio of Precipitated iron-based catalysts to H-ZSM-5. The acidity of bifunctional model catalysts was quantitatively characterized by ammonia temperature-programmed desorption (NH_3-TPD) and pyridine-adsorbed Fourier transformation infrared spectroscopy (Py-FTIR). The FTS was performed using physically mixed bifunctional model catalysts which were diluted with glass beads to keep the length of the catalysts bed constant and then charged into the fixed-bed reactor composed of stainless steel. The catalysts were activated in situ with CO_2-containing syngas at 280 ^oC and ambient pressure for 5 h, and then the FTS was conducted at 275 ^oC and 1.5 MPa using syngas for 114 h.

Results and discussion.

The activity of precipitated iron-based catalysts was not affected by the addition of H-ZSM-5, while greatly influenced the hydrocarbon distribution. The higher the acidity of the bifunctional model catalysts, the higher the C_5-C_{20} Selectivity in hydrocarbon, which is expected to be related to the linear correlation between the brønsted acid site and cracking rate. In this study, the highest hydrocarbon selectivity of C_5-C_{20} was 72.2 wt%, which was about twice as high as that of the P-Fe Catalysts.

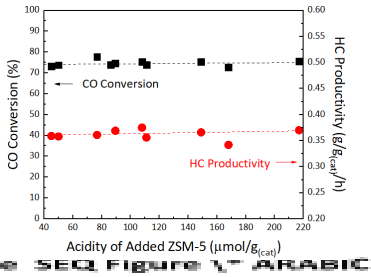

Figure SEQ Figure * ARABIC 1. The CO conversion and HC productivity as a function of acidity

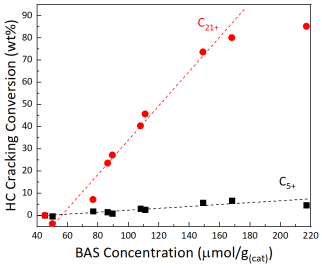

Figure SEQ Figure * ARABIC 2. The cracking rates as a function of brønsted acid sites (BAS)

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In situ and *ex situ* poisoning studies with sulphur-containing molecules using a $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst

Philipp Schwiderowski[1], Konstantinos Nikolaidis[1], Pascal Telaar[1], Patrick Diehl[1] and Martin Muhler[1]*

[1]*Laboratory of Industrial Chemistry, Ruhr University Bochum, Bochum, Germany*

[*]*Corresponding author: muhler@techem.de*

Keywords: methanol synthesis, $Cu/ZnO/Al_2O_3$, *in situ* poisoning, *ex situ* poisoning, sulphur poisoning

With the utilization of new CO_2 sources from highly polluted industrial exhaust gases, sulphur poisoning of $Cu/ZnO/Al_2O_3$ catalysts in methanol synthesis is of high interest.[1] To investigate the poisoning strengths of different S-containing impurities reported in literature,[2] long-term measurements with 6 g $Cu/ZnO/Al_2O_3$ tablet fragments and 10 ppm thiophene continuously added into the syngas feed were carried out and compared to deactivation only by thermal deactivation.

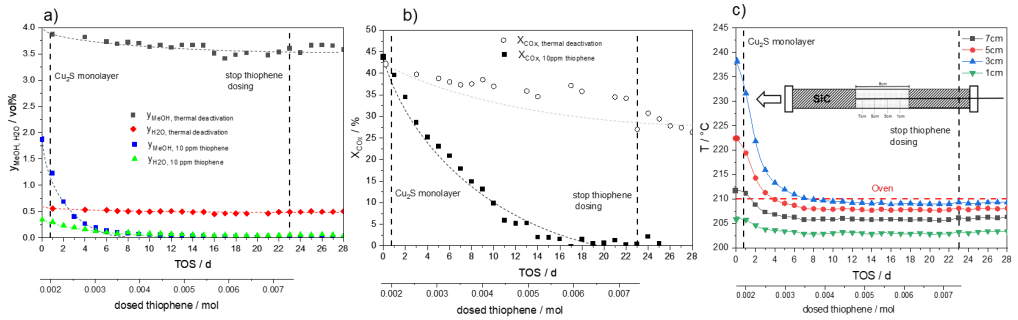

Figure 1. a) Recorded mole fractions of MeOH and H_2O at kinetically controlled conversion at 210°C for the 10 ppm thiophene and the only thermal deactivation measurement and b) COx conversion as well as c) recorded temperatures at four positions in the catalyst bed at the same conditions. All measurements were performed at 60 bar with a synthesis gas containing 10.0 vol% CO, 2,0 vol% CO_2, 78.0 vol% H_2 and 11.0 vol% N_2.

Since *in situ* long-term experiments are always time-consuming and, in addition, the post-mortem analysis of the used catalyst only permits a certain degree of poisoning (usually complete irreversible poisoning of the surface), *ex situ* poisoning studies with 1 propanethiole were carried out to gain deeper insight.[3] The poisoned catalysts were characterized using XPS, XRD, TEM, N_2O RFC, CHNS analysis as well as TEM/EDX and compared to the post-mortem characterization data obtained in the *in situ* poisoning study. By XPS in combination with XRD and CHNS analysis it was possible to identify axially decreasing sulphur content in form of Cu_2S and ZnS phases for the *in situ* poisoned samples. In addition, we identified $CuSO_4$ and $ZnSO_4$ surface layers caused by passivation of the catalyst. The self-developed *ex situ* poisoning method was identified as only involving the surface of the catalyst. We envisage to calculate the specific sulphur poisoning threshold value for $Cu/ZnO/Al_2O_3$ catalysts allowing us to deduce hypotheses about the active sites.

Acknowledgments

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Formic acid dehydrogenation catalyzed by Molybdenum-Sulfur Clusters

Carolin A. M. Stein,[1] María Gutiérrez Blanco,[2] Eva Guillamón,[2] Iván Sorribes,[2] Henrik Junge,[1] Rosa Llusar,[2] Matthias Beller.[1]

[1]*Leibniz-Institute für Katalyse e.V., Albert Einstein-Straße 29a 18059, Rostock, Germany.*
[2]*Department of Physical and Analytical Chemistry, Universitat Jaume I, 12071, Castellón, Spain.*
rosa.llusar@uji.es; Matthias.Beller@catalysis.de

Keywords: hydrogen production, formic acid, molybdenum sulfide, cluster

Introduction: The global energy crisis is driving the transition from fossil fuels to renewable energy sources. Converting wind, solar or hydropower into green hydrogen by water splitting has been proposed as a sustainable energy carrier.[1] Reconvention can be achieved by combustion or in fuel cells with water as the only by-product.[2] However, using hydrogen directly as an energy source raises several concerns related to safety and transportation issues, which necessitate the development of new hydrogen storage methods.[3] Liquid organic hydrogen carriers (LOHCs) have been considered one possible approach in safely storing hydrogen. Formic acid appears to be a good LOHC candidate considering its hydrogen content of 4.4 wt%. Moreover, FA is stable and low toxic at ambient conditions, easy to transport, handle and store.[4]

Experimental: The dehydrogenation of formic acid (FADH) enables the production of carbon monoxide-free hydrogen on demand, which is an important prerequisite for use in fuel cells. Our group has recently shown that Molybdenum PNP complexes are capable of converting FA by DH or disproportionation.[5] Furthermore, a cubane-type Mo_3S_4 cluster hydride has been shown to be active in FADH.[6] Motivated by the efficiency of Molybdenum, we have analyzed the catalytic activity of several Mo_3S_4 clusters, containing different bidentate ligands. These compounds can be easily prepared in a two-step synthesis starting from a $[Mo_3S_4Cl_4(PPh_3)_3(solv)_2]$ cluster. DH reactions were done in a double walled reactor which was equipped with a double burette manual set-up. The set-up was purged with argon several times, loaded with the catalysts and the solvent. Reactions were started by adding a mixture of FA and base.

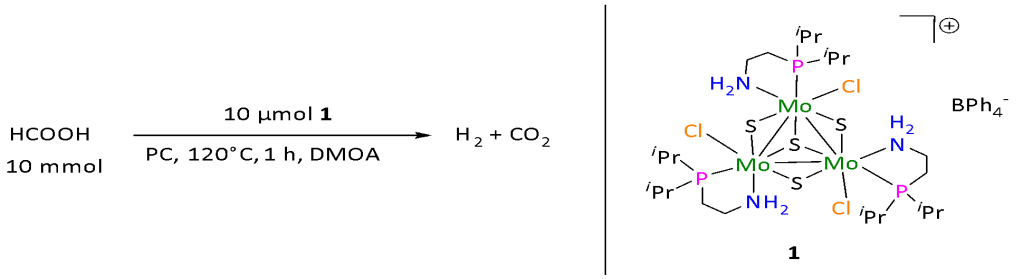

Figure 1. Formic acid dehydrogenation catalyzed by a cubane-type Mo_3S_4 Molybdenum cluster.

Results and discussion: In multiple experiments the best cluster as well as reaction conditions were identified (shown in Figure 1). Crucial for the reaction is the use of a base. All catalysts yielded carbon monoxide free hydrogen. The best results have been achieved using cluster **1.** In a solvent-free restart experiments a TON of 1900 and TOF_{1h} of 950 h^{-1} could be observed at 70°C. Complex **1** was studies further with in situ nuclear magnetic resonance spectroscopy, kinetic studies and density functional theory calculations to explain the reaction mechanism for FADH with clusters.

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3D-printed catalysts for Fischer-Tropsch reaction and the impact of Co impregnation method

B. Sutens[1*], E. Boymans[2], S. Grootjes[2], J. Lefevere[1]
[1]*Flemish Institute for Technological Research - VITO, Sustainable Materials Department, Boeretang 200, 2400 Mol, Belgium*
[2]*Netherlands Organisation for Applied Scientific Research - TNO, Biobased and Circular Technologies, Westerduinweg 3, 1755 LE, Petten, the Netherlands*
[*]*ben.sutens@vito.be*

Introduction. A shift from fossil fuel-based technologies towards renewable energy sources is becoming more and more important to meet the targets of the Paris Agreement in 2050. Especially in the aviation and shipping sectors which contributes significantly to the total anthropogenic CO_2 emissions worldwide, research towards alternative feedstocks has gained increased attention. One promising pathway includes the conversion of bio-based waste into syngas and subsequent Fischer-Tropsch synthesis into valuable liquid fuels. Conventional Fischer-Tropsch synthesis includes the use of cobalt as a catalyst in a fixed-bed reactor, typically in the shape of pellets/extrudates [1]. Although pellets and extrudates are widely commercially applied due to the simplicity and speed of the manufacturing process, a packed bed of these structures entails several drawbacks. Besides the large pressure drop that is created throughout the reactor column, mass-transfer limitations can occur due to slow diffusion to the particles core. A promising solution to overcome these drawbacks while offering a high loading per reactor volume includes the direct 3D-printing of catalyst material. Although several papers have been published involving the use of Robocasting or Direct Ink Writing (DIW) for direct 3D-printing of active species [2], limited work has been published describing the deposition of active metals on a 3D-printed support and the impact of the impregnation method.

Experimental/methodology. In this work, the impact of the Co impregnation method was studied. Cobalt on alumina catalyst structures were synthesized, characterized and tested in Fischer-Tropsch synthesis. Three different impregnation methods were evaluated, including (A) incipient wetness impregnation of the structure after printing (B) adding the metal salt precursor to the printing recipe and (C) impregnation of the alumina powder prior to 3D-printing.

Results and discussion. The physico-chemical properties of the materials were significantly influenced by the impregnation method, including the macropore volume, nanoparticle size and interaction between the cobalt and the support material. These different properties influenced the catalytic performance of the different materials, showing a clear correlation between the metal-support interaction and the activity of the catalyst. Impregnation after printing showed the highest activity whereas the activity was lowest when the cobalt salt was mixed in the print paste. A slight difference in selectivity could be attributed to the difference in cobalt nanoparticle size.

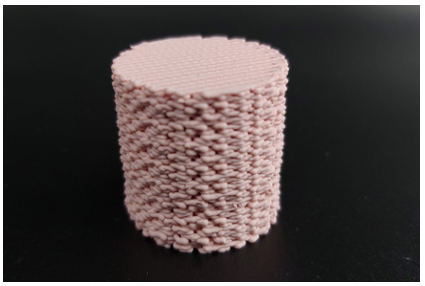

Figure 1. Picture of uncalcined 3D-printed catalyst with Co salt dispersed in the printing paste (method B).

Acknowledgments
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Plasma-catalytic CO_2 hydrogenation to methanol at room temperature and ambient pressure

Y. Wang[1], X. Tu[1*]

[1]*Department of Electrical Engineering and Electronics, University of Liverpool, Liverpool, UK*
[*]xin.tu@liverpool.ac.uk

Keywords: Non-thermal plasma, Plasma catalysis, CO_2 hydrogenation, Methanol synthesis

Introduction.
The chemical transformation of CO_2 into higher value chemicals and fuels has attracted significant interest and has been regarded as a key element of a future sustainable low carbon economy in the chemical and energy industries. However, the activation of CO_2 remains a great challenge as CO_2 is a thermodynamically stable molecule and requires a significant amount of energy for its activation. In conventional catalytic reactors, converting CO_2 to methanol requires high temperatures and pressures because of thermodynamic constraints. Non-thermal plasma (NTP) is an emerging and promising technology for CO_2 conversion under ambient conditions[1-3]. The combination of NTP with heterogeneous catalysis has great potential to generate a synergistic effect from interactions between the plasma and catalysts, which can activate catalysts at low temperatures and improve the activity and stability of the catalysts, resulting in a remarkable increase in conversion, selectivity, and yield of end-products, as well as the energy efficiency of the process. Moreover, plasma processes can be switched on and off instantly, allowing for great flexibility in decentralized chemical production using renewable energy sources, particularly intermittent renewable energy[4]. Here, plasma-catalytic CO_2 hydrogenation to methanol was investigated in a dielectric barrier discharge (DBD) reactor under ambient conditions using MgO, γ-Al_2O_3, and a series of Co_xO_y/MgO catalysts.

Experimental/methodology.
Plasma-catalytic CO_2 hydrogenation was conducted in a water-cooled DBD plasma reactor. A mixture of H_2 and CO_2 with an H_2/CO_2 ratio of 3:1 was used. The catalyst (0.5 g) was fully packed in the discharge gap. The reaction temperature was kept constant at 35 ^{o}C. All the electrical signals were recorded using an oscilloscope (Tektronix DPO 3034).

Results and discussion.
In this study, we demonstrate the potential of plasma-enhanced catalysis for CO_2 hydrogenation to methanol under ambient conditions. Packing a catalyst in a DBD plasma enhanced the conversion and narrows the product distribution of CO_2 hydrogenation. We found that the basicity of the MgO support enhanced the conversion of CO_2 compared to more acidic supports (γ-Al_2O_3). Both types of support promote the production of CO as the main product. When testing the Co_xO_y/MgO catalysts, the quantity and dispersion of metal-support interface sites are important for activity enhancement and methanol selectivity. Although CO is the main product, catalysts with higher cobalt metal loadings and good cobalt oxide dispersion favor methanol production. The most active catalyst was 15 wt % Co_xO_y/MgO, which converted 33% CO_2 and 24% H_2 near room temperature and at atmospheric pressure. This catalyst gave a 10% methanol yield, the highest among the tested materials. A further increase in the metal loading leads to larger cobalt oxide particles that block the pores, giving lower CO_2 conversion and less methanol. This work might shed light on the rational design of efficient catalysts for plasma-enhanced catalysis chemical reactions.

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Direct CO_2 Hydrogenation via Fischer-Tropsch Synthesis over Alkali-less Iron Carbide Catalyst

A. Yanagita, H. Horikoshi, S. Furuya, K. Tashiro, S. Satokawa*

Faculty of Science and Technology, Seikei University, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo 180-8633, Japan

satokawa@st.seikei.ac.jp

Keywords: Direct CO_2 hydrogenation, Fischer-Tropsch synthesis, iron carbide, alkali-less

Introduction.

To achieve carbon neutrity, conversion of CO_2 into liquid hydrocarbons (C_{5+}) as e-fuel by using catalyst has attaracted great attention. A prospective approach for this is a successive catalytic reaction of reverse water gas shift (RWGS) reaction followed by Fischer–Tropsch synthesis (FTS). However, design of the system is not easy due to the large diremption of optimal reaction temperature between RWGS and FTS, leading energy loss. Therefore, direct CO_2 hydrogenation to aquire C_{5+} via Fischer-Tropsch synthesis on one step (CO_2-FTS) is strongly desired. Iron-based catalysts is a promising candidate for CO_2-FTS, in which iron carbide is the key active species.[1] Main products of iron-catalyzed FTS are light olefins, and the addition of an alkali promoter such as K is considered essential for C_{5+} production since alkali promoters are responsible for advancing catalytic carburization[2]. On the other hand, there are few studies for the CO_2-FTS referring to a growth of carbon chains over the alkali-less iron carbide catalysts. In this study, alkali-less iron carbide catalysts were prepared and their reactivity and product compositions were investigated.

Experimental.

Alkali-less iron carbide catalyst (FeCx) was prepared by heating commercial iron(II) oxalate dihydrate at 350°C for 4 h under 30%CO/N_2 gas flow atmosphere. Alkali-modified catalyst (K-FeCx) was also prepared in the same procedure by adding KNO_3 to the raw material (K/Fe = 10, molar ratio). The addition of KNO_3 was carried out by a wet impregnation method, and then the obtained sample was dried at 120°C overnight. The catalytic activity was evaluated with pressurized fixed bed flow reactor under a reaction condition of 0.8 MPa(a), 150–340 °C, $H_2/CO_2/N_2$ = 3/1/1, and GHSV = 7400 mL h^{-1} g_{cat}^{-1}. The gaseous products and cold-trapped liquid products collected were analyzed by using a gas chromatograph (MCGC990, agilent) and a gas chromatograph mass spectrometer (GCMS-QP2010, shimadzu), respectively.

Results and discussion.

The obtained FeCx and K-FeCx catalysts were composed of mixed crystalline phases of θ-Fe_3C and χ-Fe_5C_2. Fig. 1 shows the CO_2 conversion and product selectivity of CO_2-FTS over FeCx and K-FeCx catalysts at 320°C. The CO_2 conversion of FeCx was slightly higher than that of K-FeCx, suggesting that the alkali-less FeCx is more active for CO_2 hydrogenation. However, methane formation preferencially proceeded over FeCx than that over K-FeCx. On the other hands, GCMS analysis revealed that K-FeCx tends to afford oxygenated compounds such as carboxylic acids, while such the oxygenates were negligible in case of FeCx. These results propose that the alkali-less FeCx catalyst has an extraordinary potential to produce hydrocarbons without the formation of oxygenated compounds.

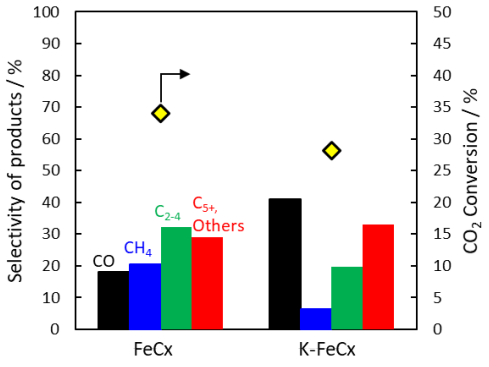

Fig. SEQ Fig. * ARABIC 1 CO_2-FTS results over FeCx and K-FeCx at 320°C. "C_{5+}, others" denotes liquid hydrocarbons and the other carbon compounds.

Acknowledgments

This study has been conducted under a contract with the New Energy and Industrial Technology Development Organization (NEDO), Japan. We would like to express our gratitude to NEDO.

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Overcoming the fundamental limitation of electrochemical methane-to-alcohol conversion via outsourced atomic oxygen – A theoretical perspective

Sungwoo Lee[1], Jaehyun Lee[2], Jun Hyuk Moon[2], Jong Suk Yoo[1*]

[1]*Department of Chemical Engineering, University of Seoul, Seoul 02504, Republic of Korea*
[2]*Department of Chemical and Biomolecular Engineering, Sogang University, Seoul 04107, Republic of Korea*
[*]*Correspondence: jsyoo84@uos.ac.kr*

Keywords: Methane-to-alcohol, conversion, atomic oxygen

Introduction. Exploiting electrocatalysis to convert methane to alcohols offers significant advantages because; (1) room temperature can be maintained throughout the process; (2) oxo-metallic sites can be continuously regenerated by forming oxygen species from the water solvent under the operating (oxidizing) condition; and (3) the water solvent is always present to extract alcohols from the catalyst surface via solvation.[1-2] Nevertheless, electrocatalytic conversion of methane to alcohols has not been very successful due to the fundamental limitation in terms of a compromise between activity and selectivity.

A good methane conversion catalyst needs to bind oxygen species extremely weakly in order to efficiently activate methane via the OH-/O-assisted mechanism. However, the consequence is that a rather high potential must be applied to form OH* and O* from water, and at this high potential, the oxygen species are prone to complete oxidation via the oxygen evolution reaction (OER) significantly decreasing the methane conversion faradaic efficiency.[3-4] In this study, we overcome the fundamental limitation using relatively abundant Fe_2O_3 as electrocatalyst for methane-to-alcohols conversion by generating active atomic oxygen (O*) on the catalyst surface via a non-electrochemical route, i.e., using carbonate ions from Na_2CO_3 as oxidant. This allows methane conversion to occur at low potential and thereby increasing the stability of the weakly bound atomic oxygen by circumventing full oxidation via OER.

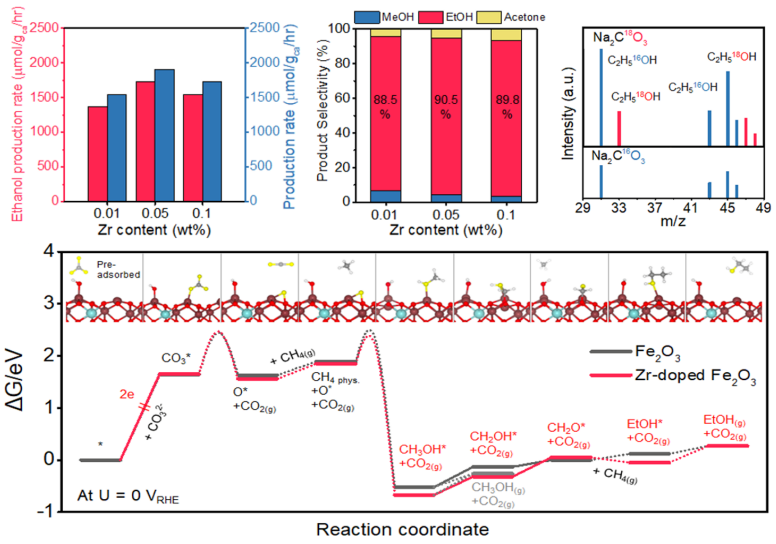

Figure SEQ Figure * ARABIC 1. Production rates of ethanol and total oxygenates for Zr-Fe_2O_3; Product selectivity for various Zr contents in Zr-Fe_2O_3; GC-MS spectrum for the ethanol product when isotope-labelled $Na_2C^{18}O_3$ is used; Calculated free energy diagrams for O* generation from CO_3^{2-} and the subsequent methane-ethanol conversion on Zr-Fe_2O_3 [0001].

Experimental/methodology. Various electrochemical characterizations, isotope labeling experiments, and DFT calculations are conducted to examine the methane-to-alcohol conversion over the synthesized Fe_2O_3 catalyst.

Results and discussion Fig. 1 shows that, an alcohol productivity of 1200 μmol/gcat/hr with the alcohol selectivity of 97.5 % (63.9 % for ethanol (1.91 USD/gal) and 33.6 % for methanol (1.45 USD/gal)) are achieved. We also adopt a zirconium doping strategy to substantially increase the alcohol productivity as well as the ethanol selectivity, achieving ~1800 μmol/gcat/hr with the ethanol selectivity of 90.5 %, as shown in Fig 1.

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Catalyst characterization incl. operando methods: experiment and theory

Outer atomic layer composition analysis of catalyst materials

T. Grehl[1*], P. Bruener[1], R. ter Veen[2]

[1]IONTOF GmbH, Münster, Germany
[2]Tascon GmbH, Münster, Germany
[*]*thomas.grehl@iontof.com*

Keywords: Low Energy Ion Scattering, surface analysis, elemental composition, outer layer
Introduction: The outer atomic layer of heterogeneous catalysts is obviously essential for the performance. Numerous analytical methods exist which look a the “surface” to analyse both the material as well as the chemical processes taking place. However, only high-resolution and high-sensitivity Low Energy Ion Scattering (LEIS) is able to quantitatively determine the elemental composition of the outer atomic layer, both for model as well as for industrial catalysts [1]. To demonstrate this unique possibiltity, we will show a range of examples of successful analysis.
Experimental/methodology: We used a Qtac 100 Low Energy Ion Scattering spectrometer, which is a specialised instrument for high-resolution and high-sensitivity quantitative elemental composition analysis of solids. The technique is insensitive to sample topography and works on insulators and conductors, making it well suited for catalyst research. Its high detection sensitivity also allows for analysis of industrial catalysts.
Using this tool and in-situ preparation techniques, catalyst materials were analysed. Ranging from single atom catalysts to automotive applications, we covered quite a range of different materials.
Results and discussion. This presentation will illustrate the possibilites arising from LEIS applications in heterogeneous catalysis. We will present the analysis results for the different materials and highlight the significance of the gained data for each of the examples. A special focus will be on explaining why LEIS could play an essential role in material characterisation in this field, as a complement to the existing surface analysis/surface science techniques.

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Operando spectroscopy explores the synergy between Pd and In_2O_3 for active CO_2 reduction catalysts

M. E. Potter[1,2*], S. Mediavilla Madrigal[2,3], P. Benito[4] and A. M. Beale[1,2]

[1]*Chemistry Department, University College London, London, UK*
[2]*UK Catalysis Hub, Research Complex at Harwell, Didcot, UK*
[3]*School of Chemistry, Cardiff University, Cardiff, UK*
[4]*Department of Industrial Chemistry, Universitá di Bologna, Bologna, Italy*

[*]*m.potter@ucl.ac.uk*

Keywords: Operando spectroscopy, CO_2 Utilisation, Methanol, EXAFS, DRIFTS

Introduction. Recently Pd/In_2O_3 systems have emerged as promising candidates for CO_2 hydrogenation to methanol. Unlike traditional Cu-based systems, Pd/In_2O_3 can achieve near quantitative methanol selectivity and are highly stable.[1,2] We have developed a novel series of Pd/In_2O_3 catalysts deposited on alumina, which despite having a fraction of the metal content, have comparable activity to pure Pd/In_2O_3 species. The precise interactions between Pd and In_2O_3 are key to creating an optimal catalyst, with the literature divided on the role of PdIn alloys. Here we present the *first operando* spectroscopic study on CO_2 hydrogenation on the synergy between Pd and In_2O_3, towards a better understanding of catalyst design.

Experimental/methodology. Our ternary $Pd/In_2O_3/Al_2O_3$ catalyst was studied with *operando* X-ray Absorption Spectroscopy (XAS) and compared with analogous Pd/Al_2O_3 and In_2O_3/Al_2O_3 systems with *operando* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). Spectra were collected under 20 bar of pressure between 30 – 250 °C, under reaction conditions, whilst the products were measured using online mass-spectrometry. XAS data of Pd and In were measured simultaneously, first under reduction activation, and then under catalytic conditions, to correlate any changes in behaviour to alloy formation and catalytic activity.

Results and discussion. XAS data under *in situ* reduction and *operando* catalytic conditions shows Pd reducing from PdO to active Pd nanoparticles (Figure 1). In remained as In_2O_3, however analysis of coordination numbers confirmed oxygen vacancies were forming on the In_2O_3 surface. During the reaction, subtle differences were seen for Pd and In, although at no point was there any significant evidence of PdIn alloy formation, suggesting the two metals operate as distinct, though likely proximate, active sites. Comparing the *operando* DRIFTS data of the monometallic and bimetallic systems strongly suggests that Pd is indeed a strong hydrogen activator but cannot efficiently activate the CO_2, which led to poor overall activity. Conversely, In_2O_3/Al_2O_3 showed continual development of activated CO_2 species on the surface but was unable to effectively activate them. As such, we will discuss the benefits of combining Pd and In_2O_3 on our unique catalyst series, the mechanistic implications this has, and how this can guide future catalyst design for CO_2 utilisation.

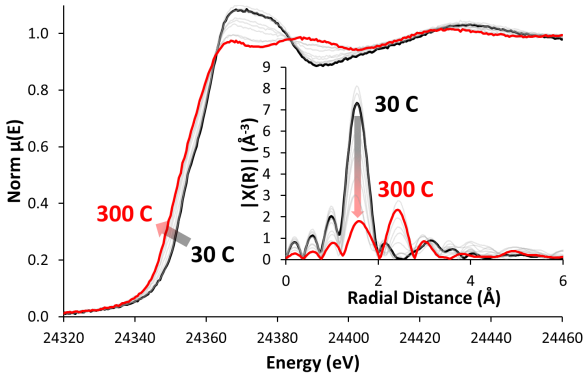

Figure 1: Showing the evolution of the Pd K-edge XAS spectra under reduction conditions.

Acknowledgments

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Hydrogen Production Mechanism in Low-Temperature Methanol Decomposition Catalyzed by Ni_3Sn_4 Intermetallic Compound: A Combined *Operando* and Density Functional Theory Investigation

Silvia Mauri[1,2*], Gianluca D'Olimpio[3], Corneliu Ghica[4], Luca Braglia[1], Chia-Nung Kuo[5,6], Marian Cosmin Istrate[4], Chin Shan Lue[5,6], Luca Ottaviano[3], Tomasz Klimczuk[7], Danil W. Boukhvalov[8], Antonio Politano[3], Piero Torelli[1].

[1]*CNR - Istituto Officina dei Materiali, TASC, I-34149 Trieste, Italy.*
[2]*Department of Physics, University of Trieste, Via Valerio 2, 34127 Trieste, Italy.*
[3]*Department of Physical and Chemical Sciences, University of L'Aquila, Via Vetoio, 67100 L'Aquila, Italy.*
[4]*National Institute of Materials Physics, Atomistilor 405A, 077125 Magurele, Romania*
[5]*Department of Physics, National Cheng Kung University, 1 Ta-Hsueh Road, Tainan 70101, Taiwan*
[6] *Taiwan Consortium of Emergent Crystalline Materials, Ministry of Science and Technology, Taipei 10601, Taiwan*
[7]*Department of Solid-State Physics, Gdansk University of Technology, 80-233 Gdansk, Poland*
[8]*College of Science, Institute of Materials Physics and Chemistry, Nanjing Forestry University, Nanjing 210037, P. R. China.*
[*]*mauri@iom.cnr.it*

Introduction. Hydrogen production from methanol decomposition to syngas (H_2 + CO) is a promising alternative route for the clean energy transition. One major challenge is related to the quest for stable, cost-effective, and selective catalysts operating below 400 °C [1]. Ni-based catalysts combine stability, catalytic activity, and low cost of raw materials, thus representing ideal candidates for industrial scaleup. One of the major challenges regards the optimization of the catalytic activity and selectivity of Ni-based alloys [2].

Experimental/methodology. In this work, we investigate the methanol decomposition mechanism of Ni−Sn intermetallic compounds with different Sn content (Ni_3Sn_4 and Ni_3Sn_2), at temperatures between 250 and 300 °C. Indeed, such a hitherto unexplored temperature range would be extremely advantageous for industrial methanol decomposition implementation. We unveiled the physicochemical mechanism ruling low-temperature methanol decomposition by combining *operando* ambient-pressure NEXAFS spectroscopy[3], synchrotron-based *in situ* X-ray photoemission spectroscopy (XPS) and high-resolution transmission electron microscopy (HR-TEM), complemented by density functional theory (DFT) calculations. The use of *operando* and *in situ* spectroscopic techniques using synchrotron radiation is particularly appropriate to monitor the status of the catalyst surface during the reaction while standard *ex-situ* investigations can only probe irreversible surface modifications, thus inevitably losing information on the various reaction steps.

Results and discussion. Our results show that a surface oxide skin imaged by HR-TEM, emerging from the natural interaction of the catalyst surface with the ambient atmosphere, plays a pivotal role in the catalytic mechanism. We also established that different amounts of Sn in the alloy strongly influence methanol decomposition selectivity, and we find an increased selectivity to H_2 with respect to secondary reaction products for Ni_3Sn_4, compared to Ni_3Sn_2. The role of surface oxide phases was also demonstrated through the analysis of pretreatment procedures of the Ni−Sn catalysts. Spectroscopic results were correlated with a semiquantitative analysis of the gas products, detected through online micro gas chromatography.

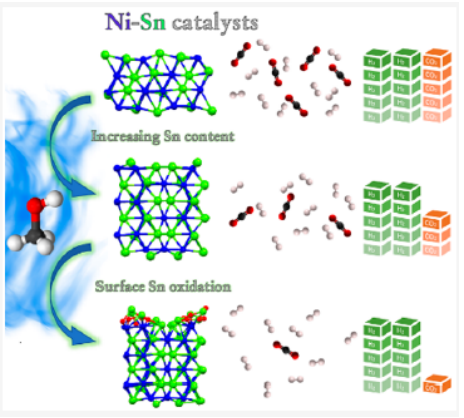

Fig.1 – Graphical abstract of the work presented

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Ductility of Pd and Pt catalysts in presence of Reactive Adsorbates

A. Ricchebuono[1*], E. Vottero[1], M. Carosso[1], A. Piovano[2], V. Crocellà[2], R. Pellegrini[3], P. Raybaud[4], C. Chizallet[4] and E. Groppo[1]

[1]*Department of Chemistry, INSTM & NIS Centre, University of Torino, via Quarello 15, Torino, I-10135, Italy*
[2]*Institut Laue-Langevin (ILL), 71 avenue des Martyrs, Grenoble, 38000, France*
[3]*Chimet SpA-Catalyst Division, Via di Pescaiola 74, Viciomaggio Arezzo, I-52041, Italy*
[4]*IFP Energies nouvelles, Rond-Point de l'Echangeur de Solaize, Solaize, 69360, France*
**e-mail: alberto.ricchebuono@unito.it*

Keywords: Palladium, Platinum, nanoparticles, reconstruction, characterization, DFT, hydrides, carbonyls.

Introduction. Ductility of metal nanoparticles promoted by adsorbates is a crucial phenomenon in catalysis, currently brought back to the spotlight by the newest developments of experimental and theoretical methods for studying nanomaterials.[1] Here we focus on two highly dispersed 5 wt.% Pd/Al_2O_3 and Pt/Al_2O_3 industrial catalysts and their interaction with two probe molecules of catalytic relevance: CO and H_2. We gathered evidences of temperature- and pressure-dependent adsorbate-induced reconstructions by coupling various experimental techniques, mainly IR spectroscopy, Microcalorimetry and Inelastic Neutron Scattering (INS), with DFT calculations.

Experimental/methodology. In situ FTIR spectra were recorded either by dosing with gas pulses, or by tuning the desorption pressure and temperature. INS spectra were recorded on the IN1-Lagrange instrument at the ILL in Grenoble. Periodic DFT calculations were performed with the VASP code, with models of extended surfaces and of clusters of various sizes (13-55) supported on γ-Al_2O_3 surface models.

Results and discussion. IR spectra collected while dosing small incremental CO pulses on Pd/Al_2O_3 indicate that, at high coverage, bridged carbonyls on the Pd(100) facets decrease in favor of top ones (Fig. 1A). This phenomenon entails an unexpected increase in the heat of adsorption of CO, measured by Microcalorimetry. This suggest that CO is triggering a surface reconstruction entailing the corrugation of the Pd(100) facet into novel defective adsorption sites. We are performing DFT calculations to inspect the impact of CO adsorption on the stability of "low index" and corrugated "high index" Pd crystal facets.

The vibrational fingerprints (collected with FT-IR[2] and INS[3]) of the hydrogenous species generated at the surface of Pt/Al_2O_3 under H_2 atmosphere reveal a different distribution of surface Pt-H species at high and low H_2 coverage (Fig. 1B). The DFT simulation of vibrational and thermodynamic properties of this system led to a rationalization of the observed phenomenon,[3] with a massive reconstruction of Pt nanoparticles in the catalyst, modifying both their morphology and their degree of interaction with the support.[3]

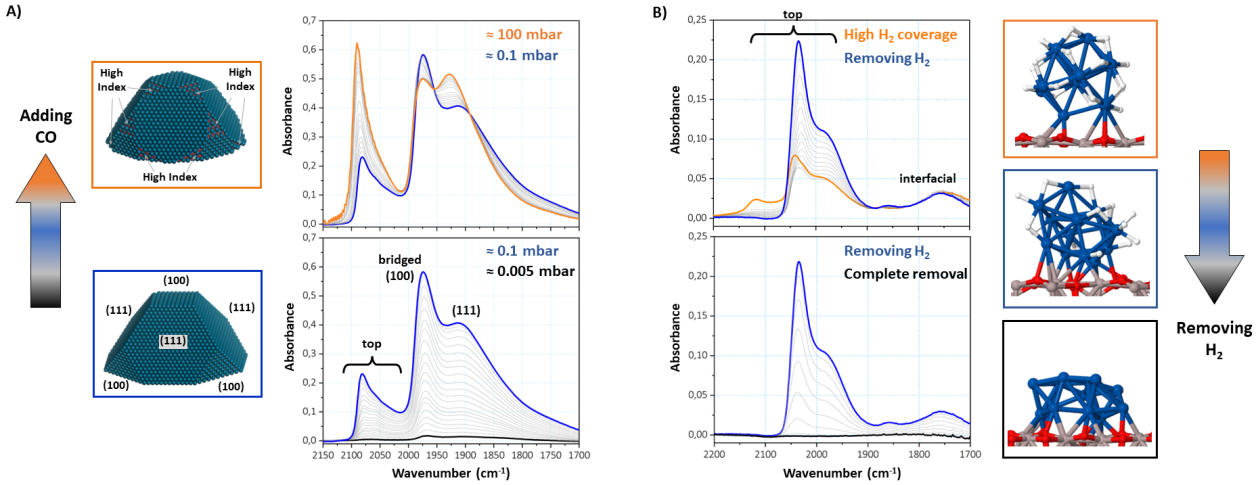

Fig. 1. FT-IR spectra collected while increasing CO coverage on the Pd/Al_2O_3 catalyst (A) and while decreasing H_2 coverage on the Pt/Al2O3 catalyst (B). The two reconstructions are visualized thanks to a few molecular models.

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Composition-Driven Differences in Active Site Speciation and Behavior in Methane to Methanol Oxidation of Copper Exchanged Chabazite

A. Brenig[1,2], J.W.A. Fischer[3], D. Klose[3], G. Jeschke[3*], J.A. van Bokhoven[1,2*] V.L. Sushkevich[2*]

[1]*Institute for Chemical and Bioengineering, ETH Zurich, Zurich, Switzerland*
[2]*Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute, Villigen, Switzerland*
[3]*Laboratory of Physical Chemistry, ETH Zurich, Zurich, Switzerland*
[*]*gunnar.jeschke@phys.chem.ethz.ch*, *jeroen.vanbokhoven@chem.ethz.ch*, *vitaly.sushkevich@psi.ch*

Introduction. The wasteful handling of natural gas in the oil and gas sector in combination with the strive for resource efficiency has animated research efforts to identify effective methods to convert retained CH_4 into high-value commodity chemicals such as CH_3OH. [1,2] Direct, low-temperature CH_4 oxidation by Cu exchanged zeolites via chemical looping has proven to be a particularly promising technology as a result of its scale flexibility and exceptional CH_3OH selectivity. Among the different zeolite topologies, Cu exchanged chabazite (Cu-CHA) is of special interest due to its superior CH_3OH yield. [3] However, attempts at industrial implementation are impaired by the lack of knowledge regarding the influence of the Si/Al ratio and the Cu-loading on the Cu active site speciation governing the redox behavior and CH_3OH selectivity of the material. [4] This is further aggravated by the fact that information about the site-specific kinetic properties is missing. The present work aims at identifying the composition dependent Cu speciation by determining characteristic spectroscopic fingerprints and at elucidating their distinct kinetic behavior. Structure-activity relationships are established by correlating these results to the redox activity and CH_3OH selectivity of the bulk material.

Experimental/methodology. Four Cu-CHA materials differing in Cu speciation were prepared by deliberately varying the Si/Al ratio and Cu-loading. The results of plug flow reactor (PFR) reactivity tests were correlated to *in situ* X-ray absorption near edge structure (XANES) and *in situ* Fourier-transform infrared (FTIR) spectroscopy experiments. The observed differences in redox behavior and CH_3OH selectivity of the samples were linked to the variation in Cu speciation, which was established by means of *in situ* FTIR of adsorbed NO as well as *ex situ* Raman, *ex situ* photoluminescence (PL), *operando* ultraviolet-visible diffuse reflectance
(UV-Vis), and *operando* electron paramagnetic resonance (EPR) spectroscopy.

Results and discussion. Samples exhibiting a low Si/Al ratio and Cu content predominantly host isolated Cu^{2+} ions, whereas oxygenated Cu centers are favored at high Si/Al ratio and/or Cu-loading. The latter includes monomeric $[CuOH]^+$ as well as dimeric $[Cu_2(\mu\text{-}O)]^{2+}$ and $[Cu(\mu\text{-}1,2\text{-}O_2)]^{2+}$ species. Compared to Cu-oxo compounds, bare Cu^{2+} active sites are characterized by a slower reaction rate, which is reflected in a shift of the redox activity profile to higher reaction temperatures. Simultaneously, these active centers feature a higher CH_3OH-based Cu efficiency and CH_3OH selectivity than their oxygenated counterparts do. This indicates that the high activity of $[Cu_2(\mu\text{-}O)]^{2+}$ and $[Cu(\mu\text{-}1,2\text{-}O_2)]^{2+}$ moieties comes at the expense of material selectivity. The findings (summarized in Figure 1) highlight the influence of the composition on Cu active site speciation, which ultimately determines the material properties in CH_4 oxidation.

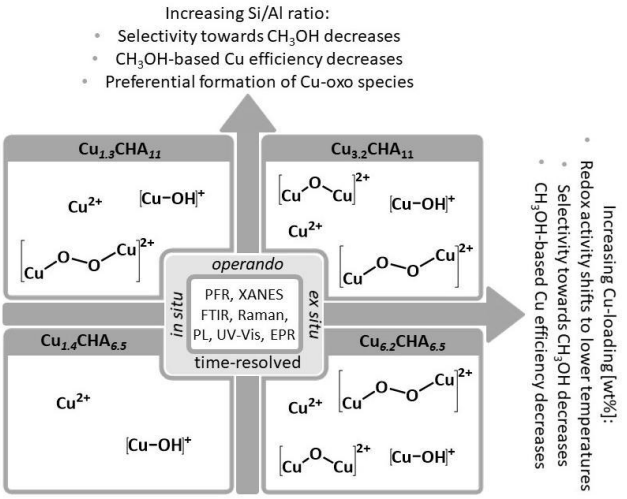

Figure 1. Cu speciation of different samples as well as the influence of the Si/Al ratio and the Cu-loading on the material behavior in CH_4 oxidation.

Acknowledgmentes

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Decisive roles of peripheral promoters in promoting methanol selectivity of CO_2 hydrogenation over Cu-based catalysts

N. Phongprueksathat[1], S.R. Docherty[2], G. Noh[2], C. Copéret[2], A. Urakawa[1*]

[1]*Catalysis Engineering, Department of Chemical Engineering, Delft University of Technology, Delft, The Netherlands*
[2]*Department of Chemistry and Applied Biosciences, ETH Zürich, Zurich, Switzerland*
[*]*A.Urakawa@tudelft.nl*

Introduction The nature of the active site of the industrial $Cu/ZnO/Al_2O_3$ catalysts is still under debate despite 50 years after the discovery. The structures of active Cu-ZnO synergy under working conditions were prevalently reported [1]; however, their roles in the mechanistic aspects are still ambiguous. Moreover, interfacial metal sites such as Ga and In at the periphery of Cu nanoparticles also play a similar role in boosting methanol selectivity over Cu-based catalysts [2].
Experimental The copper-based catalysts with single-site promoters ($Cu\text{-}M/SiO_2$, M = Zn, Ga, and In, **Fig 1a**) were prepared precisely via surface organometallic chemistry (SOMC) [3]. *Operando* transient DRIFTS and isotopic transient experiment (SSITKA) have shed light on the roles of surface intermediates and M sites.
Results and discussion. All the $Cu\text{-}M/SiO_2$ catalysts proceeed through the same reaction pathways and common formate intermediate on Cu. The M sites at the periphery of Cu particle stabilize formate species spillovering from Cu for faster hydrogenation (weakened C–O bond and strengthened C–H bond). Moreover, the transfered formate from Cu to M sites suppresses its decomposition to CO over Cu, and improves methanol selectivity. Based on significant kinetic isotope effects (KIE), the methanol activation towards formation/desorption to methanol is the rate-limiting step, and there were slight KIE for formate hydrogenation and negligible KIE for H_2 dissociation and formate formation.

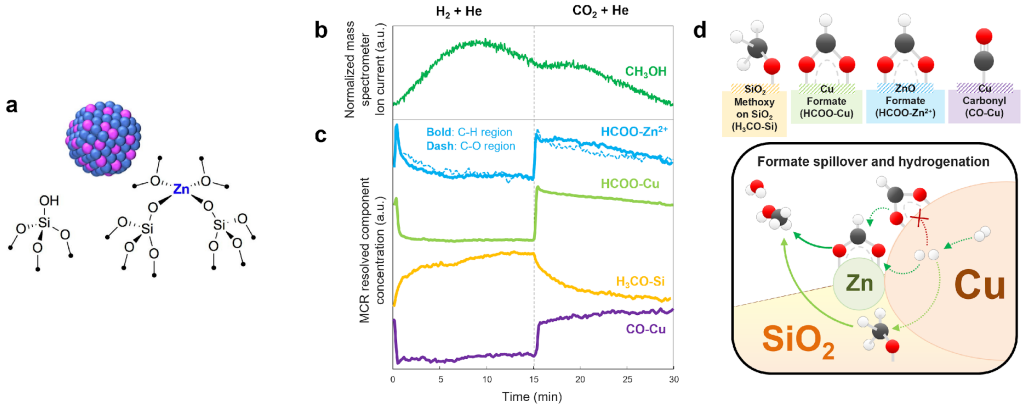

Fig. 1 a Structure of $Cu\text{-}Zn/SiO_2$ prepared via SOMC reported elsewhere [3]. Transient responses of surface species and gas products during switching from He + CO_2 to H_2 + He over $Cu\text{-}Zn/SiO_2$ catalysts at T = 230°C, P = 20 bar, F_{total} = 10 NmL min^{-1}: **b** CH_3OH signal from MS. **c** Surface species concentration profiles obtained from multivariate curve resolution (MCR). **d** The proposed reaction pathway for formate hydrogenation via spillover to Zn sites.

The mechanisms proposed for the $Cu\text{-}Zn/SiO_2$ is shown in **Fig 1d**. Overall, formate over Zn is more reactive (higher methanol formation rate), while the formate spillover toward Ga is more facile (higher methanol selectivity). The mechanistic insights from the model $Cu\text{-}Zn/SiO_2$ catalyst unveiled the nature of highly debated Cu-ZnO synergy that plays a crucial role in defining the catalytic activity of the industrial $Cu/ZnO/Al_2O_3$ catalysts. This also highlights the essence of Cu-M interfacial sites in determining selectivity, which is important for the rational design of nano-structured catalysts for selective CO_2-to-methanol.

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Tracking the evolution of Ni-based single atom catalysts for the CO_2 electroreduction reaction: an *operando* XAS study assisted by machine learning techniques

A. Martini[1*], J. Timoshenko[1], D. Hursán and B. Roldán Cuenya
Department of Interface Science, Fritz-Haber Institute of the Max-Planck Society, 14195 Berlin, Germany.
E-mail: martini@fhi-berlin.mpg.de

Keywords: CO_2RR, Ni-based Single atom catalysts, X-ray Absorption Spectroscopy, Machine Learning.

Introduction.
In the last decade, Ni and nitrogen co-doped carbons have attracted attention as promising catalysts for the CO_2 electroreduction reaction (CO_2RR) exhibiting high CO_2-to-CO conversion activities, comparable with those of noble metal catalysts [1]. In these systems, N atoms are incorporated in the carbon support forming a binding site for the singly-dispersed Ni species [2]. However, it is worth noting that a large number of different structural motifs can coexist in these systems and evolve during the CO_2RR process, making the identification of actual active sites and interpretation of the CO_2RR reaction steps difficult to realize experimentally. We addressed this issue by combining *operando* X-ray absorption spectroscopy with advanced data analysis. In particular we show how the combination of unsupervised and supervised machine learning approaches is able to decipher Ni K-edge XANES spectra of these systems, disentangling the contributions of different Ni sites coexisting in the working catalyst. Moreover, thorugh this approach, we obtained quantitative structural information about the local environment of the active Ni species, including their interaction with adsorbates, allowing us to shed more light on the complex dynamic mechanism of the CO_2 electroreduction.

Experimental/methodology.
Operando time-resolved XANES data were used to unveil the local structure around Ni sites in their *as prepared* states, but also under realistic working conditions during CO_2RR. A multi-step approach has been used for the interpretation of the collected XANES data. First, we identified the number of different coexisting Ni species, their corresponding kinetic profiles and XANES spectra using unsupervised machine learning methodologies, such as the principal component analysis combined with a multivariate curve resolution technique [3]. In the second step, we deduced the atomistic structures for each of the identified species through a XANES fitting procedure, realized exploiting a supervised machine learning approach [4]. Finally, we validate the predicted structures processing the corresponding EXAFS spectra *via* Reverse Monte Carlo simulations [5], taking into account the structural disorder in the local environment around the identified Ni species.

Results and discussion.
Our results confirm that the single Ni sites are the active species for the CO_2RR, but also reveal their dynamic, heterogeneous nature and adaptation to the reaction conditions. In particular, our data suggest that the local environment around Ni is directly affected by the interactions between the Ni site and CO adsorbates. We found that the initial state of our catalysts (before the CO_2RR), can be represented by a six coordinated model with four planar Ni-N bonds and two axial O atoms. The CO_2RR induces a local structural distortion of the Ni site in the N doped carbon matrix, with the progressive substitution of both the O atoms with a CO adsorbate. Overall, these results demonstrate the potential of XAS spectroscopy in combination with advanced data modelling to access an unprecedented level of understanding of a complex multi-component catalytic system, yielding novel insights into the birth of Ni-active sites for the CO_2RR reaction.

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HERFD-XAS study on molecular adsorption states of strong base metal oxide cluster catalysts

T. Matsuyama[1,2], H. Nagakari[2], S. Kikkawa[2], N. Kawamura[2], K. Higashi[2], N. Nakatani[2], S. Yamazoe[1,3]

[1]*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Tokyo, Japan*
[2]*Japan Synchrotron Radiation Research Institute (JASRI), Hyogo, Japan*
[3]*Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, Tokyo, Japan*
[*]*yamazoe@tmu.ac.jp*

Keywords: Metal Oxide Cluster, Base Catalysts, HERFD-XAS

Introduction. Metal oxide clusters consisting of group-V transition metals such as $[M^{V}_{6}O_{19}]^{8-}$ (M^{V}=Nb, Ta) have a unique strong base catalyst that is comparable to MgO. They catalyze Knoevenagel condensation reactions and CO_2 fixation reactions without being deactivated by molecular adsorption[1]. In this study, we investigated unique molecular adsorption states on $[M^{V}_{6}O_{19}]^{8-}$ by high-energy-resolved fluorescence detection X-ray absorption spectroscopy (HERFD-XAS) which enables direct observation of the crystal field of Nb and Ta correlated with local structural change[2]. We have acquiredHERFD-XANES spectra of Nb K- and Ta L_3-edges and successfully observed changes in the crystal field attributed to molecular adsorption for the first time.

Experimental/methodology. Tetrabutylammonium salts of $[M^{V}_{6}O_{19}]^{8-}$ were synthesized by a microwave-assisted hydrothermal method in reference to the literature[3] and characterized by infrared spectra and electrospray ionization mass spectra. HERFD-XANES spectra at Nb K-edge was measured with Laue-type X-ray emission spectrometer at SPring-8 BL12XU and Those at Ta L_3-edge with Rowland-type X-ray emission spectrometer at SPring-8 BL39XU.

Results and discussion. Molecular adsorption states of $[Nb_6O_{19}]^{8-}$ (Nb6) were studied by pre-edge peaks in Nb K-edge HERFD-XANES spectra (Fig.a). When 1% CO_2 gas with N_2 balance and acid-base indicators as adsorbents were added to Nb6 DMF solution, the intensity of pre-edge peaks in both XANES spectra decreased compared to the pristine Nb6. These results indicate that CO_2 and protons adsorbed to the same base sites with an increase in their octahedral symmetry. Ta L_3-edge HERFD-XANES spectra (Fig.b) also reflected d-orbital splitting affected by molecular adsorption to $[Ta_6O_{19}]^{8-}$ (Ta6), and the increasement of splitting width of the white line by CO_2 adsorption was observed. From comparison with reference samples combined with theoretical calculations, we conclude that Ta6 activated CO_2 accompanied with the increase of the octahedral symmetry near the active site of Ta6 (Fig.c).

Figure (a) HERFD-XANES spectra at Nb K-edge and (b) those at Ta L_3-edge. (c) Expected molecular adsorption states.

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Operando IR-GC-MS Investigations for Catalytic Recycling of Polyolefins on zeolites

K.A. Tarach[1], M. Akouche[3], J. Martinez-Triguero[2], K. Pyra[1], F. Rey[2], V. Valtchev[3], J.-P. Gilson[3], K. Góra-Marek[1]

[1] *Faculty of Chemistry, Jagiellonian University in Kraków, Poland*
[2] *Instituto de Tecnologia Quimica (UPV – CSIC), Valencia, Spain*
[3] *Laboratoire Catalyse et Spectrochimie (LCS), Normandie University, Caen, France*
[*] *kinga.gora-marek@uj.edu.pl*

Introduction. Polypropylene and polyethylene find numerous applications in the household and industry. Currently, only 1% of waste is chemically reprocessed to recover the olefinic building blocks, thus meeting the criteria for a true circular economy. In this context, the process of catalytic decomposition of polymers into value-added products is an important element in meeting the societal challenge of plastic disposal.

Zeolites are some of the most important heterogeneous catalysts in oil refining and petrochemistry. They offer nonpareil properties such as high surface areas, high thermal and chemical stability and finally well-defined topology with uniform micropores hosting numerous and strong acid sites. The confined adsoption of reactants in micropores provides exceptional selectivities in catalytic processes. Uniqe shape selectivity property is often untouched when bulky reactants are involved. The presence of severe diffusion limitations dramatically reduces the catalytic potential of zeolites. Several different approaches concerning their synthesis and modifications have been developed to zeolites with additional meso- and macroporous feature. The synthesis methods are gathered around two main routes: top-down approaches concerning the preferential extraction of silica or alumina from the zeolite structure and bottom-up methods employing templates to synthesize so-called nano-zeolites or embryonic zeolites (EZ). The latter are X-ray amorphous materials, collected in the early stages of zeolite synthesis, but their active sites are more accessible, allowing the conversion of large reactants. Similarly to zeolites wide pores zeolites and the mesoporous counterparts currently employed as the catalysts in oil refining and petrochemistry, the EZ extend the range of applications to the processing of heavy oil fractions and related feedstocks such as polyolefins.

Methodology. The catalytic cracking of polypropylene over EZs and purely crystalline counterparts was monitored by *operando* FT-IR coupled with CG-MS to simultaneously measure catalytic activity, product selectivity and deactivation process.

Results and discussion. On the EZ, polypropylene produces the lowest C_3-C_4 (gaseous) and C_5-C_6 (liquid) fractions but more of the C_{7+} than native H-ZSM-5 catalyst as the lower confinement in micropores inhibites recracking reactions. The textural properties of EZ are responsible for advanced hydrogen-transfer processes resulting in a much higher paraffin (70 %) selectivity. In a sense, EZ-ZSM-5 behaves more like a FAU than an MFI structure. 2D COS IR spectroscopy monitoring of coke formation and combustion highlight the role of silanols in the coke retention. The unique microporosity qualifying EZ as wide pore material allows the efficient contact between reactants (coke and oxygen) due to not restricted the diffusion of oxygen.

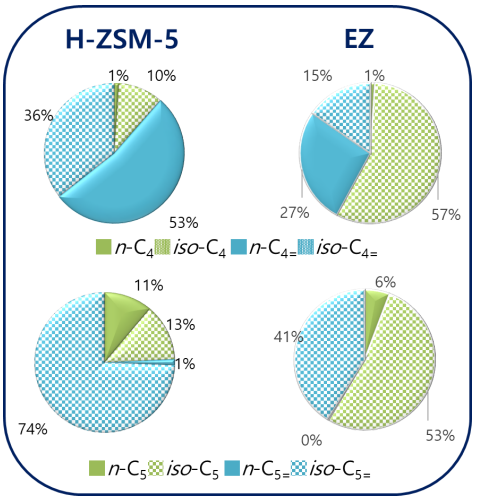

Fig. 1. Product distribution in C_4 and C_5 fractions.

Acknowledgments

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Development of Metal-Ion DNP NMR Technique for Characterization of MOF-based Catalysts

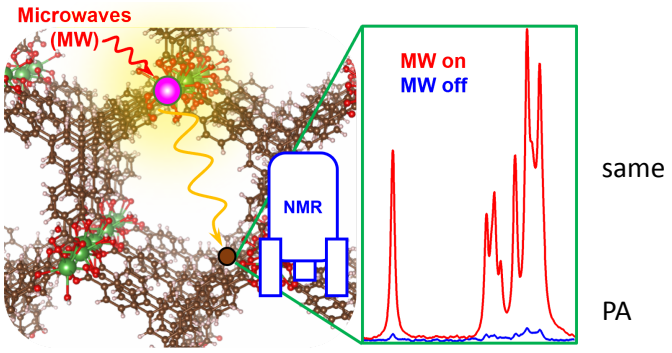
I. B. Moroz[1*], Y. Feldman[2], M. Leskes[1]

[1]*Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovot, Israel*
[2]*Department of Chemical Research Support, Weizmann Institute of Science, Rehovot, Israel*
[*]*michal.leskes@weizmann.ac.il*

Keywords: Metal-organic framework catalyst, metal-ion DNP, solid-state NMR

Introduction. Metal-organic frameworks (MOFs) are crystalline porous materials featuring a unique combination of properties, including ultrahigh surface area, structural diversity and adjustability. This renders MOFs a perfect platform for the fundamental understanding of the catalysts and for the rational design of new catalytic solids [1]. The catalytic studies on MOFs rely on a broad spectrum of characterization techniques, and solid-state Nuclear Magnetic Resonance (ssNMR) is of great importance: it provides information on the MOF structure and on the interactions of MOF, as a host, with adsorbed reagents, as guests [2]. Despite considerable success, NMR application is limited by its inherently low sensitivity. It hinders characterization of nuclei present in small quantities (in active sites or in adsorbed reagents), having low natural abundance (^{13}C, ^{17}O, ^{15}N etc.) or exhibiting extremely broadened NMR signals (metal nuclei). Significant improvement in NMR sensitivity has been achieved in the last two decades by the introduction of Dynamic Nuclear Polarization (DNP). In DNP we introduce unpaired electrons that possess a 3-4 orders of magnitude higher polarization than nuclei and apply microwave irradiation to transfer this polarization to nuclei of interest and enhance their NMR signal. In standard DNP experiment, the catalyst is impregnated with a solution of organic radicals – *exogenous polarizing agents* (*PA*). Despite its effectiveness, this approach may be destructive for highly reactive active sites and not suitable for studying host-guest interactions, since the pores are filled with the PA solution. An alternative approach developed in our group for energy storage materials characterization is *endogenous metal-ion DNP* (MIDNP), in which paramagnetic metal ions doped into materials structure play the role of PAs [3]. Here, we extend this approach to MOFs with an ultimate goal of facilitating NMR application to MOF-based catalysts and providing new insights on their catalytic properties.

Experimental/methodology. To demonstrate the applicability of *endogenous MIDNP* to MOFs, we synthesized a series of samples with the MOF structure and various amount of paramagnetic dopant. The electron spin properties of paramagnetic dopant were characterized by EPR spectroscopy and their efficiency was investigated using commercially available Bruker 400 MHz DNP-NMR system.



Results and discussion. Endogenous MIDNP was applied to MOFs for the first time to our knowledge, leading to 30-fold enhancement of NMR signals of MOF linkers, while the pores stay empty for reagents adsorption and the sites present on the pore surface remain intact. Furthermore, we discuss the parameters that affect MIDNP efficiency in MOFs, such as concentration of the PA, the presence of O_2 in the pores, the mobility in MOFs, and suggest the optimal conditions for the DNP-enhanced NMR experiments. Overall, our results demonstrate that MIDNP approach is a promising tool for studying catalytically active MOF-based systems and it can potentially be extended to other porous catalytic systems.

Acknowledgments
I.B.M. is grateful to the Sustainability and Energy Research Initiative (SAERI) fellowship for financial support

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What is my catalyst doing? New Insights into Rh/P - catalysed olefin hydroformylation from multi-nuclear *operando* FlowNMR Spectroscopy

Alejandro Bara-Estaún,[1,2] Catherine Lyall,[1,2] John Lowe,[1,2] Ulrich Hintermair*[1,2,3]

[1] *Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom*
[2] *Dynamic Reaction Monitoring Facility, University of Bath, Bath BA2 7AY, United Kingdom*
[3] *Institute for Sustainability, University of Bath, Bath BA2 7AY, United Kingdom*
* *u.hintermair@bath.ac.uk*

Introduction

The speciation of a molecular catalyst during turnover contains a wealth of information, including the effectiveness of precursor activation, amount of inactive or dormant states, and population of in-cycle reaction intermediates. Access to this information requires a non-invasive, quantitative *operando* technique that is compatible with the reaction conditions. We have developed a multi-nuclear, high-resolution FlowNMR spectroscopy setup[1] that may analyse air-sensitive homogeneous catalytic systems during turnover under high temperature and pressure conditions in real time to combine reaction progress monitoring (rates & selectivities) with quantitative catalyst tracing in a single experiment.[2]

Results and discussion

We will briefly discuss the technique and point out some critical considerations for its effective use,[3] including hardware aspects as well as the importance of flow effects on continuous NMR acquisition.[4] As an example of application, we will present some of our recent work on using this setup to interrogate the industrially relevant hydroformylation reaction of terminal alkenes catalysed by Rh/PR_3 catalysts.[5] In addition to demonstrating the difference between *in situ* and true *operando* analysis, we show how the many different catalyst intermediates formed in this dynamic system may not only be observed but even quantified across different reaction conditions to provide catalyst speciation maps[6] that explain the mechanistic origin of ligand effects in this widely used reaction.[7]

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Using NAP-XPS to elucidate when the surface of cobalt and promoted cobalt Fischer-Tropsch catalysts can become oxidised by water

K. L. MacIntosh[1], N. Novruzova[1], A. Zachariou[1], M. Almashnowi[1], E. Olivas[1], A. Marsh[1], S. K. Beaumont[1]*

[1]*Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK*
[*]*Simon.Beaumont@durham.ac.uk*

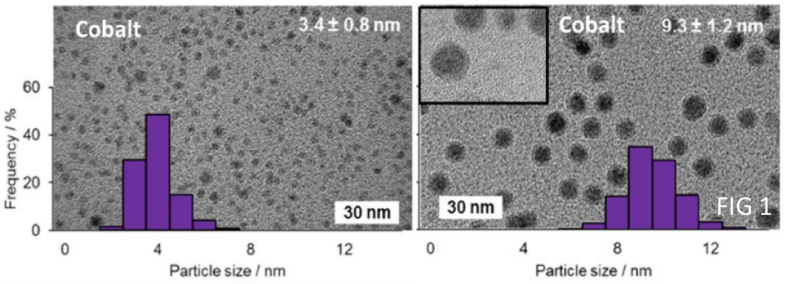
Keywords: Fischer-Tropsch Synthesis; water deactivation; oxidation; cobalt; promoters

Introduction. Fischer-Tropsch (FT) chemistry, while originally focussed on producing synthetic fuel, is now rapidly finding itself an attractive prospect for non-fossil derived chemical production from other sources of syngas (waste plastic pyrolysis gas, electrocatalysis with renewables, gasified biomass). One still poorly understood aspect of this important transformation is the extent to which water can cause deactivation.

While bulk oxidation (except in the presence of alumina) doesn't happen thermodynamically [1], and diligent XAFS measurements have shown water doesn't cause bulk oxidation in Co/SiO_2 [2], the idea of surface oxidation is still prevalent in the literature, and may play an important role in the design of processes if it is a deactivation pathway [3,4]. The process is also hard to separate in rate measurements from sintering effects that may also be induced by water [5], and further complicated by the well-known different susceptibility of different sized metal particles to oxidation [6,7].

To address this, we have prepared size-controlled nanoparticles of Co (a widely used FT catalyst), tested them for FT activity and investigated their surface oxidation state with NAP-XPS (near ambient pressure X-ray photoelectron spectroscopy) using Diamond Light Source's capabilities to go to high mbar pressures of water. Being a surface sensitive technique (in contrast to bulk techniques employed in other studies) allows us to elucidate the impact of water on the reoxidation of FT catalysts' surfaces.

Experimental/methodology. Small (3 nm) and large (9 nm) colloidal nanoparticles were prepared by decomposition of $Co_2(CO)_8$ as reported elsewhere [9]. Some samples were modified by the addition of a precious metal promotor. These were tested in a fixed-bed reactor after deposition on SiO_2 or used for NAP-XPS after deposition at sub particle-monolayer coverages on a Si wafer. Samples were oxidised and reduced *in situ* at the B07 endstation, then exposed to increasing pressures of water.



Results and discussion. Typical cobalt samples prepared are shown in Figure 1. Catlaytic tests confirmed the expected results from literature that large particles were more active than small particles (only the larger particles show conversion of CO (7.9 ± 1.1 %) at 200 °C, and the addition of precious metal promotor increases conversion. After *in situ* reduction in the NAP-XPS system both pure cobalt samples could not be oxidised by 5mbar water, however oxidation did occur in the presence of water for the precious metal promoted sample (Figure 2). This is a striking result as precious metals are typically added to promote reduction, but here also appear to promote oxidation by water.

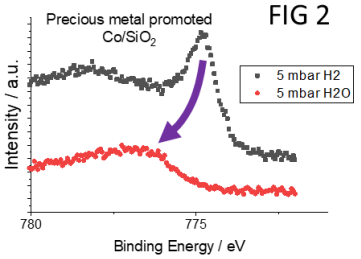


FIG 2

Acknowledgments

The authors gratefully acknowledge Diamond light source (SI27736 & SI28832) and experimental assistance from the beamline scientists Georg Held, Federica Venturini and Alex Large.

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Operando Raman spectroscopy in the liquid phase for the characterization of Diols conversion on layered catalysts

Hamza Bekkali[1], Philippe Boullay[2], Guillaume Clet[1*]

[1] *Normandie Univ, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, 6 Bd Marechal Juin,14050 Caen, France.*
[2] *Normandie Univ, ENSICAEN, UNICAEN, CNRS, CRISMAT, 6 Bd Marechal Juin,14050 Caen, France.*
[*] *guillaume.clet@ensicaen.fr*

Keywords: Raman spectroscopy, Operando, Layered materials, Liquid phase characterization.

Introduction.

The development of new catalysts for biomass conversions induces new demands on the materials as reactions are often carried out in the liquid phase, catalysts should be water tolerant and allow sufficient access of the reagents to the active sites because derivatives from biomass often involve the transformation of large substrates such as saccharides or diols [1]. These constraints on the catalysts imply that they should also be characterized in similar conditions. However, unlike reactions in the gas phase, the operando characterization of catalysts is rarely undertaken in the liquid phase and adequate methodologies for such characterization still need to be developed.

Experimental/methodology.

Operando Raman spectroscopy has thus been used here to evaluate layered catalysts for the conversion of diols. Diols can be used as a representative model reactant, and we showed recently that acidic layered materials $HNbMoO_6$ and $HNbWO_6$ were efficient catalysts for 2,5-hexanediol cyclodehydration to 2,5-dimethyltetrahydrofuran in liquid phase [2,3]. Niobate layered materials will be compared here with their tantalate equivalents $HTaMoO_6$ and $HTaWO_6$, working at different temperatures in a batch autoclave adapted for simultaneous Raman measurements.

Results and discussion.

In a first stage, Raman spectroscopy was used to evaluate and compare the acidity of the solids by adsorption of a liquid probe molecule. Then, operando Raman was specifically carried out in liquid medium to monitor both the reactant intercalation and its effective reaction on the layered materials. Raman spectroscopy then allows to determine the conversion and reaction parameters, through the use of the reactants and products specific bands, but also to follow the evolution of the solid catalysts in the course of the reaction. For each of these Raman characterization stages, adequate spectroscopic analysis methodologies were developed.

The layered materials proved to be efficient catalysts for the transformation of the 2,5-hexanediol polyoxygenate without any preliminary thermal activation step. The tantalates appear less active than the niobates while molybdates are more active than tungstates. Differences in acidity do not account for these different activities. Nevertheless, the chemical changes in the materials composition are also accompanied by changes of the interlayer spacing affecting at the same time the intercalation of the diol. Our results point out the importance of the ability of the material to accommodate the reactant between its layers and its large influence on their reactivity.

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Nanoscale Chemical Diversity of Coke Deposits on Metal Nanocatalysts Visualized by Tip-Enhanced Raman Spectroscopy

M. Filez,[1,2] C. Detavernier,[2] H. Uji-I,[3] M. B. J. Roeffaers[1,*]

[1] *cMACS group, KU Leuven, Leuven, Belgium*
[2] *Conformal Coating of Nanomaterials group, Ghent University, Ghent, Belgium*
[3] *Division of Molecular Imaging and Photonics, KU Leuven, Leuven, Belgium*
**maarten.roeffaers@kuleuven.be*

Introduction. Coke formation is a prime cause of catalyst deactivation.[1] During hydrocarbon conversion, non-selective side reactions occur which lead to the formation of undesired carbonaceous products. These species eventually anchor on the catalyst surface as carbon deposits, i.e. 'coke', which block the active sites and inhibit further reaction.[2] To regenerate coked catalysts, high-temperature O_2 calcination treatments are applied to burn coke deposits[3,4] into CO_2 and H_2O, thus further accelerating climate disruption.

To increase process efficiencies and remediate our environment, next generation catalysts need to be designed which prevent coke formation. Yet, foundational knowledge gaps still exist on the origins of coke formation, thus not offering rationally-guided concepts to redesign today's catalysts.[5] The missing key for knowledge build up is the lack of nanoscale characterization tools which can chemically identify coke very locally at the catalyst surface, to elucidate their origin and link their nature to the catalyst structure.

Methodology. Here, we apply tip-enhanced Raman spectroscopy (TERS) as a nanoscale chemical probe to identify and localize the coke species on a post-mortem model metal catalyst (Fig. 1a). Therefore, axially-aligned Pt nanorods (l x w x h = 200 x 10 x 10 nm^3, Fig. 1b) supported on SiO_2 are exposed to a 15 min C_3H_8 flow to perform propane dehydrogenation reaction (C_3H_8 = C_3H_6 + H_2 + coke), leading to coke deposition.

Applying conventional TERS on such relevant metal-oxide supported catalysts is very challenging – if not unfeasible – since no sufficient Raman enhancement is obtained in the gap between the plasmonic tip and the insulating support.[6] Here, this issue is overcome by using specialized Ag nanowire tips: by cutting the tips, a spherical apex is generated which contains nanoscale defects that inherently boost plasmonic enhancement, independent of the nature of the support. This approach enables first-of-its-kind nanoscale metrology of coke deposits on relevant model metal catalysts, with 20 nm spatial resolution.

Results and discussion. An exemplary TERS spectrum collected at one surface location of the coked Pt/SiO_2 catalyst shows a diversity of Raman peaks, directly proving the rich chemical diversity of coke deposits at the nanoscale (Fig. 1c). The local TERS enhancement yields very sharp peaks, enabling unparalleled coke characterization compared to conventional bulk Raman spectra. Three classes of carbon-based materials can be distinguished: (I-orange) nanocrystalline graphite built-up of ordered, 2D-stacked graphene layers, (II-red) amorphous sp^2-bound carbon, and (III-green) C-rich polymeric carbons, all having different origins.

Clustering analysis allows to sort the hyperspectral TERS map into three zone with different averaged spectral features (Fig. 1d): (A-blue) Pt lines with high coke concentration of high disorder, (B-yellow) an off-Pt zone with intermediate coke concentration and medium disorder, and (C-green) a support with low coke concentration and relatively ordered graphite. This analysis suggests that disordered coke species formed on Pt spill over to the support where they react and grow into more ordered, graphitic coke. This approach paves the way to fundamental knowledge build up on deactivation by coke and smart catalyst redesign.

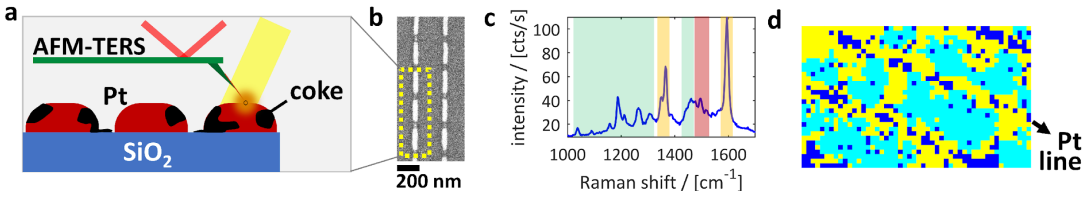

Fig 1. (a) Schematic overview of TERS experiment, (b) top view of Pt/SiO_2, (c) TERS spectrum, (d) TERS clustering map.

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Monitoring the structural evolution of multicomponent catalysts for selective olefin oxidation by complementary *operando* techniques

Linda Klag[1], Thomas L. Sheppard[1,2], Jan-Dierk Grunwaldt[1,2*]

[1]*Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany* [2]*Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany* [*]*grunwaldt@kit.edu*

Introduction. Selective oxidation of olefins is a key reaction in chemical industry, leading to important intermediates and various products.[1] These include selective propylene and isobutene oxidation to acrolein and methacrolein, respectively, both typically catalysed by bismuth molybdate based multicomponent systems.[2] Such catalysts exhibit a complex phase ensemble, forming composites of selective, active, promoting and inert phases.[3] However, the role of individual (mixed) metal oxide phases and their interaction is still in its infacy and strongly discussed.[4,5] To close the knowledge gap between functionality of model systems (*e.g.*, Bi-Mo-O) and industrially-applied catalysts (*e.g.*, Bi-Mo-Fe-Co-W-K-Si-O), studying Bi-Mo-Co-Fe-O as a 4-component system is very promising, as it provides a suitable representation of complex metal oxide phase mixtures and superior catalytic performance.[6] Since catalyst performance is highly sensitive towards *e.g.* synthesis conditions, we investigate the influence of preparation method and elemental composition on catalyst activity and selectivity. Advanced synchrotron *operando* techniques are crucial to monitor the dynamic and synergistic interplay of the various phases of the catalyst in its working state. As this affects several time and length scales, we present both integral and spatially-resolved insights into structure and activity of such 4-component Bi-Mo-Co-Fe-O catalysts.

Experimental/methodology. Bi-Mo-Co-Fe-O catalysts differing in promotor content were prepared by flame spray pyrolysis (FSP) and hydrothermal synthesis (HTS). Catalysts were tested for several days on stream at different oven temperatures and WHSVs (70/14/8/8 % $He/O_2/C_nH_{2n+2}/H_2O$; n = 3, 4). Catalyst characterization was performed by complementary synchrotron-based *operando* XRD (BM01, ESRF, Grenoble, FR), XAS (ROCK, Soleil, Saint-Aubin, FR), and Raman spectroscopy to cover both crystalline and amorphous phases. Moreover, we performed spatially-resolved characterization with (simultaneous) acquisition of spatially-resolved activity and temperature profiles.

Results and discussion. Both preparation methods and elemental catalyst composition of Bi-Mo-Co-Fe-O directly influenced catalytic performance. This could be explained by the formation of various metal oxide phases regarding the inital catalyst state, leading to different phase (trans-) formations upon catalyst activation as seen by *e.g.* synchrotron XRD (Fig. 1). For the FSP catalysts, an Mo content of ≥ 50 mol% resulted in high, controllable activity and high selectivity to acrolein or methacrolein. Conversely, lower Mo content led to extremely active catalysts and strong hot-spots in the catalyst bed (Fig. 2). Finally, direct comparison of phase evolution during selective propylene and isobutene oxidation allowed to gain general conclusions on structure-activity relations and thus a more profound understanding of the working principles of such complex catalyst systems.

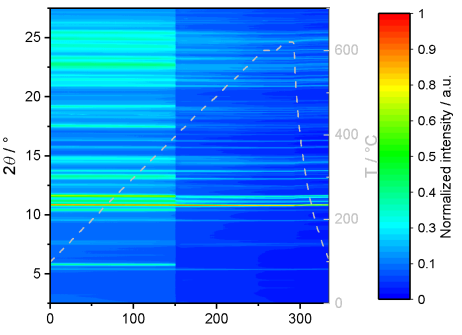

Figure SEQ Figure 1. ARABIC 1: Structural evolution of a Bi-Mo-Co-Fe-O catalyst (FSP) derived from XRD during selective isobutene oxidation.

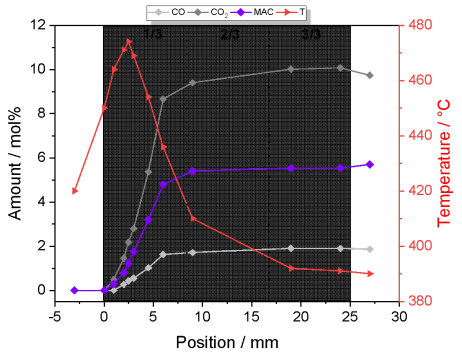

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Figure 2: T-/c-profiles in the catalyst bed during selective isobutene oxidation.

Critical Role of Water in Preferential Carbon Monoxide Oxidation over Pt-Fe Catalysts: Operando XAS/DRIFTS Approach

Ilia I. Sadykov[1,2], Frank Krumeich[2], Dennis Palagin[3], Davide Ferri[1], Igor V. Plokhikh[1], Jeroen A. van Bokhoven[2,1], Maarten Nachtegaal[1], and Olga V. Safonova[1]*.

[1]*Paul Scherrer Institute, 5232 Villigen, Switzerland*
[2]*ETH Zurich, 8092 Zürich, Switzerland*
[3]*Delft University of Technology, 2600 AA Delft, Netherlands*
**olga.safonova@psi.ch*

Introduction. Water accompanies hydrogen production and purification via the main industrial routes, such as the reforming of hydrocarbons and the water-gas shift reactions.[1] Highly efficient preferential carbon monoxide oxidation (PROX) is vital for the purification of hydrogen from the traces of poisonous carbon monoxide. Water strongly affects PROX Pt-Fe catalysts but the nature of its action remains unclear.

Experimental/methodology. In this work, we were able to decipher the water effect on the reactivity of supported Pt-Fe PROX catalysts using operando X-ray absorption spectroscopy and operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) coupled with in-line mass spectrometry following catalytic state, conversion, and selectivity of active sites in real-time.[2]

Results and discussion. Our work shows that the addition of water both during the reduction pretreatment of the catalysts at high temperatures and during the catalysis is beneficial and can lead to a significant increase in carbon monoxide conversion preserving high selectivity. We found that pretreatment of Pt-Fe catalysts under the 98 vol.% H_2 – 2 vol.% H_2O (hydrogen-steam) gas mixture up to 473 K and the direct addition of water into the reaction mixture enables to achieve the highest activity among reported Pt-Fe catalysts.

The kinetic experiments, including those with ^{18}O-labeled water, in combination with operando DRIFTS (**Figure 1**), show that water hydroxylates the redox-active iron phases during high-temperature pretreatment in the hydrogen-steam mixture. This pretreatment creates active iron-associated hydroxyl groups with enhanced reactivity towards carbon monoxide chemisorbed on platinum nanoparticles.

A quantitative correlation between the catalytic activity of Pt-Fe/γ-Al_2O_3 catalysts and Fe^{2+} concentration, obtained using operando X-ray absorption spectroscopy,[2] shows that the number of carbon monoxide molecules converted per each individual active Fe^{2+} site increases after the reduction pretreatment in the hydrogen-steam mixture. Density functional theory (**Figure 1**) provides a model demonstrating that hydroxylation of oxidic iron species stabilizes the $FeO_x(OH)_y$/Pt interface. Hydroxyl groups bound to redox-active iron constitute active sites (**Figure 1**), allowing ambient temperature selective catalytic oxidation.

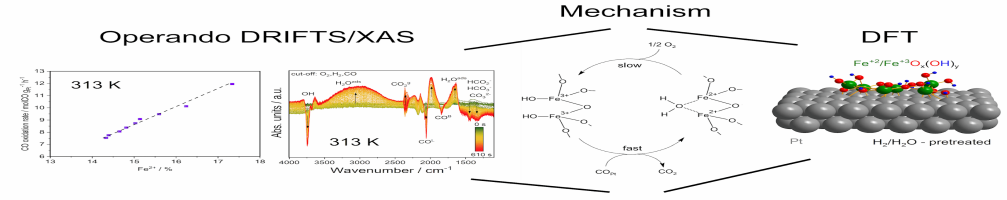

Figure 1. The results of operando XAS/DRIFTS experiments with steam-activated Pt-Fe/γ-Al_2O_3 catalyst, the proposed mechanism of PROX reaction, and the DFT model of the active $FeO_x(OH)_y$/Pt interface.

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Tracking catalyst structures from synthesis to reaction via pair distribution function on a Ag@H-BEA zeolite

F. Müller*, N. Simitsis[2], R. Palkovits[2], M. Zobel[1]

[1]RWTH Aachen University, *Institute of Crystallography, Aachen, Germany*
[2]RWTH Aachen University, *Institute of Technical and Macromolecular Chemistry, Aachen, Germany*
mueller@ifk.rwth-aachen.de

Keywords: PDF, Beta Zeolite

Introduction.
For sustainable catalysis and in light of changing feedstocks to renewable sources, novel catalytic systems are required. We have designed an Ag@H-BEA bifunctional catalyst system for the selective synthesis of dimethoxymethane by non-oxidative dehydrogenation of methanol, based on the synthesis of Cu@H-BEA [1]. To tackle the structure-activity-correlation of Ag loading of 1 to 20 wt% and catalyst pretreatments (calcination, reduction) with catalytic activity, structural insight into the nature of the active sites, the structure of the support and its relation to the activity of the overall catalytic system are vital. The pair distribution function (PDF) is able to provide this access into both the short-range order and local structure of the zeolite and the supported Ag nanoparticles.

Experimental/methodology.
The atomic PDF is a histogram of all interatomic distances in the sample, calculated from high energy X-ray scattering data. The PDF is well suited to structurally characterize non-crystalline, disordered and nanostructured materials beyond common crystallographic approaches. Further, occupancies or thermal motion, as well as local coordination environments and nanoparticle diameter can be refined in the PDF [2]. Having pushed the quality of laboratory PDF data in recent years on diffractometers [3], we can now achieve detailed insight into supports and active species of heterogeneous catalysts in our laboratory. [4] Here, we employ a STOE STADI P powder diffractometer in transmission geometry, using monochromatic Ag $K\alpha_1$ radiation and a MYTHEN2 4K detector.

Results and discussion.
Our XRD and PDF results show that the H-Bea zeolite structure is affected by Ag loading and treatment conditions, such as reducing atmosphere. The active species can be described as Ag fcc nanoparticles. The zeolite features rather low crystallinity and undergoes increasing restructuring, the higher the Ag loading, reflected in splitting of few Bragg peaks. Structural refinements of the zeolite show an increase of the average domain size from about 3 nm for the unloaded zeolite to about 4 – 5 nm for the reduced and spent catalysts. Further we correlate pore sizes in PDF and N_2-physisorption analysis.
Hereby, we show that a rational design of future catalysts crucially depends on characterizing the evolution of catalyst structures from synthesis via reaction to spent state with advanced scattering techniques.

Acknowledgments
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Effect of H_2 pressure on the carbon path of methanation reaction on Co/γ-Al_2O_3: Transient isotopic and operando methodologies

M.A. Vasiliades[1], R. Crous[2], D. Moodley[2], T. Botha[2] and A.M. Efstathiou[1,*]

[1]*Department of Chemistry, Heterogeneous Catalysis Laboratory, University of Cyprus, Nicosia, CY*
[2]*Research and Technology, Energy Operations and Technology, 1 Klasie Havenga Street, Sasolburg 1947, SA*
[*]*A.M. Efstathiou: efstath@ucy.ac.cy*

Keywords: methanation reaction, SSITKA, transient CO hydrogenation-DRIFTS, Co/γ-Al_2O_3.

Introduction

Fischer-Tropsch synthesis (FTS) is regarded as one of the most effective and key technologies to assist in future decarbonization of various industries by utilizing syngas derived from renewable feedstocks. SSITKA is established as one of the most advanced kinetic techniques to quantify the composition of adsorbed phase (surface coverage, θ) of active reaction intermediates, and to estimate rate constants of individual elementary reaction steps on a working catalyst surface via microkinetic modeling of rival mechanisms [1]. Also, SSITKA-DRIFTS determines the chemical structure of active and inactive reaction intermediates [1]. The present work established a powerful protocol based on SSITKA-Mass Spectrometry, SSITKA-DRIFTS, and transient CO-DRIFTS hydrogenation coupled with kinetic modelling to further promote fundamental understanding of the H_2 pressure effect on important kinetic parameters of mainly the methanation reaction at 230 °C and 1 atm on a commercially relevant Co/γ-Al_2O_3, and in particular that of θ_H, for the first time [1].

Experimental/methodology

The step-gas concentration switch 5 vol% ^{12}CO/x vol% H_2/Ar (5 h, 230 °C) ⟶ 5 vol% ^{13}CO/x vol% H_2/1 vol% Kr/Ar (t) (x = 10-50) at the entrance of a microreactor was applied (X_{CO} < 20%), followed by 3-min Ar purge, transient isothermal hydrogenation (TIH, 50% H_2/Ar, 7 min), and temperature-programmed hydrogenation (TPH). Transient CO hydrogenation - DRIFTS with kinetic modelling, and SSITKA-MS were used to esimate the dependence on P_{H2} of the θ_H and site hydrogenation activity (k_{eff}) of the two linear-types adsorbed CO-s [1].

Results and discussion

The surface coverages (θ) of reversibly adsorbed CO-s and active -CH_x (C_α) were found to be influenced slightly only by P_{H2}, as opposed to the θ of inactive carbonaceous species, hydrogenated at 230 °C to CH_4 (under TIH), named C_β (-C_xH_y) - "soft carbon", and those hydrogenated at T > 230 °C (TPH), named C_γ ($C_{\gamma1}$-$C_{\gamma3}$) - "hard carbon" (**Fig. 1A**). A large influence of P_{H2} was also observed on: (i) TOF_{CO} and TOF_{CH4} (s^{-1}); (ii) the effective rate constant of CH_x-s hydrogenation (k_{eff}=kθ_H), and (iii) the mean lifetime of adsorbed CO ($\tau_{CO,}$ s) and CH_x (τ_{CHx}). Transient exchange rate profiles (μmol g^{-1} s^{-1}) of active $^{12}CH_x$-s for $^{13}CH_x$-s were estimated for the first time (**Fig. 1B**), as an additional descriptor parameter of SSITKA, aiming to provide fundamental understanding of the mechanism of methanation reaction without kinetic modelling. A shoulder becomes evident when P_{H2} increases, result that supports the existence of more than one kind of CH_x-s hydrogenated to CH_4, and linked to chain-growth [1]. SSITKA-DRIFTS followed by TIH (**Fig. 1C**) and coupled with kinetic modelling, highlighted the k_{eff} dependence on P_{H2} for each of the two linear-types adsorbed CO-s identified (after IR band deconvolution). The influence of P_{H2} on θ_H was establish for the first time (**Fig. 1D**). The increase of θ_H (P_{H2}=600 mbar) by a factor of ~ 4.5 relative to that at the lowest P_{H2} (120 mbar) was used to explain the variation of TOF_{CH4} and k_{eff} with P_{H2} [1].

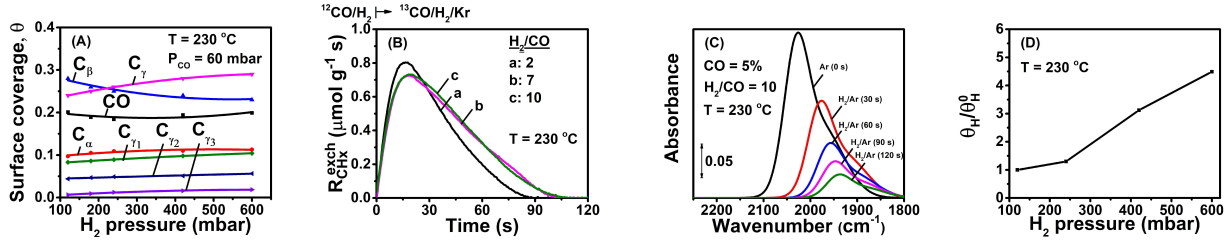

Fig. 1: (A) Surface coverages of *active* CO-s and CH_x-s (C_α), and of *inactive* C_β and C_γ (sum of $C_{\gamma1}$, $C_{\gamma2}$, $C_{\gamma3}$); (B) Dynamic evolution of the transient rate (μmol g^{-1} s^{-1}) of $^{12}CH_x$-s exchange; (C) CO-DRIFTS spectra recorded in Ar and 50% H_2/Ar gas flow; (D) Dependence of θ_H (at P_{H2}) with respect to the reference θ^0_H (at P_{H2}=0.12 bar) on P_{H2}.

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Photocatalytic set-up for in situ and operando ambient pressure X-ray photoelectron spectroscopy at the MAX IV laboratory

Alexander Klyushin[1]*, Manoj Ghosalya[2], Esko Kokkonen[3], Calley Eads[1], Rosemary Jones[3], Naresh Nalajala[4], Chinnakonda S. Gopinath[4], Samuli Urpelainen[2]

[1]*MAX IV Laboratory, Lund University, Box 118, Lund, 22100, Sweden*

[2]*Nano and Molecular Systems Research Unit, University of Oulu, Oulu, 90014, Finland*

[3]*Division of Synchrotron Radiation Research, Department of Physics, Lund University, Box 118, Lund, 22100, Sweden*

[4]*Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Pune, 411008, India)*

[*]*alexander.klyushin@maxiv.lu.se*

Keywords: Photocatalysis, APXPS, Photo-ALD, solar simulator.

Introduction. Processes driven by solar radiation play a crucial role in life on Earth. Nowadays, replacing fossil fuels with clean and renewable energy sources is one of the most important challenges for modern human civilization. Natural photoassisted solar reactions can convert solar energy into usable chemical energy by driving reduction and oxidation processes via generation of electrons and holes, respectively, upon irradiation of the photocatalyst. Photo-assisted atomic layer deposition (Photo-ALD) is a less studied approach to facilitating selective area ALD. ALD is an extremely versatile thin film deposition process that is currently used in many steps within the microelectronics process flow and is also attracting increasing interest in other industrial areas.

Experimental/methodology. The APXPS endstation at SPECIES beamline at MAX IV is designed to perform in-situ and operando XPS experiments in a controlled atmosphere at pressures up to 20 mbar [1]. Research areas of interest include catalysis, material and surface sciences, environmental chemistry, and atomic layer deposition. However, there is a lack of APXPS studies that pair synchrotron light with external light sources. Here we will introduce and discuss the use of solar irradiance with APXPS cells and provide a series of scientific case studies that serve to illustrate the usefulness of the concept.

Results and discussion. One such scientific case is hydrogen production via water splitting sunlight is used to induce a photocatalytic reaction at a photoactive surface. We study pristine Ni@NiO/$NiCO_3$ core-shell nanostructures as photocatalysts and characterize their post-annealing variants. During illumination, it was observed that the metallic Ni peak vanishes, and the new peak appeared that we've assigned to NiOOH. However, no changes were observed in the Ni 2p peaks from NiO and/or $NiCO_3$.

Another example lies in an under-utilized technique called photo-ALD which allows spatially selective ALD to be carried out. Herein, we tested the photo-ALD set-up using a hafnium tert-butoxide ($Hf(OtBu)_4$) precursor and UV light to produce HfO_2 on a Si (100) wafer. Throughout the deposition, XPS was recorded with time-resolved snapshot mode tracking a series of pertinent core-levels every 15 s. Results show HfOx is being formed during the UV pulse.

In summary, the APXPS endstation at SPECIES beamline has two ambient pressure cells, a standard cell for catalysis, redox chemistry, etc. and an ALD cell for ALD research. Solar simulator and UV-lamp can be used with both cells, as we've demonstrated. These combinations provide a unique platform to conduct experiments to study the electronic structure of matter under IR/visible/UV radiation and at different pressure ranges and gas mixtures.

Acknowledgments

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Comparison of newly identified $[Cu\text{-}O\text{-}Cu]^{2+}$ and $[CuOH]^{+}$ Sites in Cu-CHA and Cu-MOR Zeolites for Selective Methane Oxidation to Methanol

D. Plessers[1*], A. J. Heyer[2], H. M. Rhoda[2], M. L. Bols[1], R. A. Schoonheydt[1], E. I. Solomon[2], B. F. Sels[1]

[1] *Center for Sustainable Catalysis and Engineering, KU Leuven, Leuven, 3000, Belgium*
[2] *Department of Chemistry, Stanford University, Stanford, CA 94305, U.S.A*
[*] *dieter.plessers@kuleuven.be*

Keywords: copper zeolites, partial methane oxidation to methanol, site-selective & operando spectroscopy

Introduction.

Cu-exchanged zeolites are promising candidates for a mild, selective oxidation of methane to methanol, which is a major goal of modern chemistry [1]. Three zeolite topologies are particularly promising and have dominated literature since 2005: MFI, MOR and CHA. In the past, our group managed to identify and characterize a mono-(μ-oxo) dicopper(II) species ($[Cu\text{-}O\text{-}Cu]^{2+}$) in MFI [2] and two slightly different $[Cu\text{-}O\text{-}Cu]^{2+}$ species in MOR [3] as active sites at temperatures around 423-473 K. Recently, we added two new active sites to this catalogue of fully characterized active sites.

Experimental/methodology.

After ion exchange with copper(II) acetate and calcination, the copper-zeolites were autoreduced in helium at elevated temperatures, activated with N_2O or O_2 and reacted with methane at 473 K. Active site characterization occurred via a combination of DR-UV-Vis, in-situ resonance Raman (rR) , EPR, MCD and XAS spectroscopies. Kinetic parameters of the active site for methane oxidation were obtained by operando UV-Vis. DFT models (B3LYP) were constructed in agreement with the spectroscopic and kinetic results.

Results and discussion.

First, in Cu-CHA zeolites, we fully characterized a $[Cu\text{-}O\text{-}Cu]^{2+}$ that is present after activation with N_2O or O_2 [4]. This species exhibits a clear absorption band around 22400 cm^{-1} in the DR-UV-Vis spectra, which decays upon methane reaction. An analysis of resonance Raman vibrations and their ^{18}O isotope shifts obtained after activation with $^{18}O_2$ was key in revealing the $[Cu\text{-}O\text{-}Cu]^{2+}$ structure.

Second, in Cu-MOR zeolites, we elucidated a $[CuOH]^{+}$ active site that is characterized by a broad OH^{-} to Cu(II) charge transfer band at 20700 cm^{-1}, a $g_{\|}$ = 2.27 feature in EPR and a Cu-O stretch of 750 cm^{-1} in resonance Raman ($\Delta^{18}O$ = 35 cm^{-1}) [5].

This catalogue of active sites in Cu-MFI, Cu-MOR and Cu-CHA allowed us to compare their reactivity in methane oxidation by monitoring the decay of the characteristic absorption bands of $[CuOH]^{+}$ and $[Cu\text{-}O\text{-}Cu]^{2+}$ during reaction with methane. This revealed three key elements that determine reactivity: zeolite confinement influencing methane adsorption [6], lattice-imposed geometrical constraints reminiscent of the entatic state concept in metalloprotein chemistry [4] and higher metal nuclearity leading to delocalization of the electron gained in the hydrogen atom abstraction step and increasing reactivity.

These principles could open up new applications that require lower reaction temperatures, such as the ambient capturing of CH_4 as a negative emission technology. Additionally, these structure-reactivity relationships are more generally applicable to redox catalysis over transition metal ion exchanged zeolites.

Acknowledgments

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In situ MAS NMR spectroscopy reveals the mechanism of methane coupling to hydrocarbons over copper-containing mordenite

Mikalai A. Artsiusheuski[1,2], René Verel[1], Jeroen A. van Bokhoven[1,2,*], Vitaly L. Sushkevich[2,*]

[1]*Institute for Chemistry and Bioengineering, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland*

[2]*Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*

[*]*jeroen.vanbokhoven@chem.ethz.ch, vitaly.sushkevich@psi.ch*

Keywords: copper zeolites, methane oxidation, methanol, methane coupling, in situ MAS NMR, MTH, MTO.

Introduction. The transformation of methane to valuable chemicals at small-scale levels is an attractive strategy for valorization of abundant, yet currently underutilized natural gas resources. Direct methane oxidation to methanol via chemical looping over copper-containing zeolites is considered as a promising process [1-2]. Previously, we demonstrated that apart from methane partial oxidation to methanol, C-C coupling takes place in the course of methane conversion over copper-containing zeolites at elevated temperature leading to formation of C_2+ hydrocarbons [3]. In the current work, we applied *in situ* MAS NMR spectroscopy to identify the mechanism of the formation of higher hydrocarbons.

Experimental/methodology. Different reaction pathways may lead to the C-C bond formation: i) the direct coupling of methane over copper (I) sites ii) the methanol-to-hydrocarbon (MTH) pathway, in which methanol formed by methane oxidation over copper(II)-oxo sites subsequently transforms into hydrocarbons and iii) the Koch carbonylation of the methanol or methoxy species with carbon monoxide into methyl acetate and its further conversion [3-5]. To differentiate the various possible mechanisms, we investigated the conversion of different mixtures containing ^{13}C-labelled and nonlabelled reactants over copper-containing mordenite and traced ^{13}C isotope label in products.

Results and discussion. Figure 1 summarizes the reaction network observed for transformation of methane and its partial oxidation products over copper-containing mordenite. Methane reaction with copper(II)-oxo sites yields partial oxidation products, namely methanol, methoxy species, and dimethyl ether. At elevated reaction temperature the partial oxidation products may undergo further transformations. Thus, the MTH process can take place, where conversion of methoxy species over acid sites leads to the formation of methylsubstituted cyclopentenyl cations, which form the hydrocarbon pool working as co-catalyst in methanol transformation to hydrocarbons. In the presence of carbon monoxide, methoxy species are transformed into surface acetates via the Koch carbonyation reaction. The acetates themselves are converted into methylsubstituted benzenes at elevated temperature, forming another type of hydrocarbon pool as compared to the pure methanol conversion. Specific adsorption of methane over copper (I) takes place, however, no further transformation of this complex to C_{2+} hydrocarbons was observed up to 773 K.

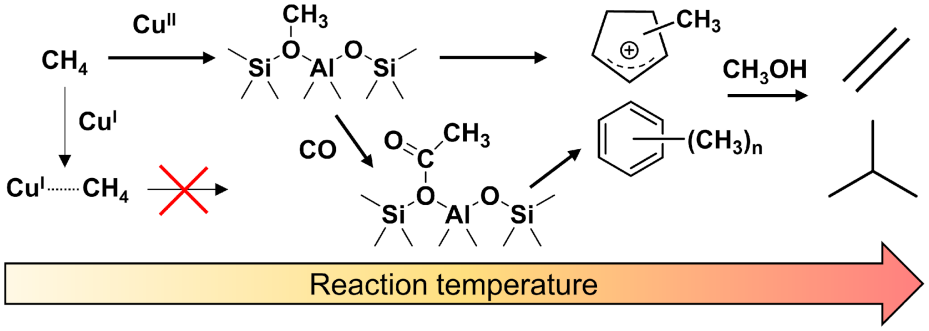

Figure 1. Chemical transformation observed in the course of methane conversion over oxygen-activated copper-containing mordenite

The study provides the mechanism of methane partial oxidation and MTH reactions at the molecular level and demonstrates a possibility to combine the mentioned processes over multifunctional copper-containing zeolitic materials, thereby offering attractive eventual route for methane valorization.

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Active carbenium species direct olefins selectivity in the methanol-to-olefins process

L. Maggiulli[1,2*], M. Nachtegaal[1], O. Kröcher[1,3], J.A. van Bokhoven[1,2], D. Ferri[1]

[1]*Paul Scherrer Institut (PSI), Forschungsstrasse 111, 5232 Villigen (Switzerland)*
[2]*Institute for Chemical and Bioengineering (ICB), Department of Chemistry and Applied Bioscience, ETH Zürich, Vladimir-Prelog-Weg 1-5/10, 8093 Zürich (Switzerland)*
[3]*Institute of Chemical Sciences and Engineering (ISIC), EPFL, 1015 Lausanne (Switzerland)*
[*]*luca.maggiulli@psi.ch*

Keywords: Methanol-to-olefins, zeolites, operando spectroscopy

Introduction. The methanol-to-olefins (MTO) process will be a green alternative for the olefins and fuel industry of the future. Notoriously the reaction pathway involves the formation of hydrocarbon species that operate as active sites in the so-called hydrocarbon pool (HCP) mechanism.[1] Olefins and aromatic hydrocarbons represent the main two classes of molecules that can convert methanol within the respective catalytic cycle through consecutive methylation and cracking/dealkylation steps upon mediation of Brønsted acid sites of zeolites.[2] Quantitative correlations between olefins and active centers in the HCP are often drawn through ^{13}C labelling and laborious extraction of retained species post-reaction. Here we have developed an operando IR spectroscopy approach with transient MeOH flow that allows identification of active carbenium ions which correlate linearly with olefins for three representative zeolite topologies.

Experimental/methodology. We have employed diffuse reflectance IR spectroscopy (DRIFTS) and a custom-built flow reactor cell that ensures isothermal operation by design and probing of the catalyst along the vertical cross section of the bed.[3] Methanol was modulated asymmetrically through an automatic switching valve system synchronized with micro-GC sampling: this was done by alternating a short section of methanol flow with a longer period in which the catalyst was exposed solely to an inert Ar flow, in a cyclic manner. Within the second step of the cycle weakly adsorbed molecules are removed leading to IR spectra free of non-desirable absorption peaks which can hinder their interpretation. ZSM-5 (MFI), SSZ-13 (CHA) and Ferrierite zeolites with similar Si/Al ratio (~11) were employed.

Results and discussion. We identified different carbenium species by their features in the ν(C=C) region of the IR spectrum in the three zeolites. In Ferrierite we report a limited formation of bulky aromatics in favor of acyclic alkyl cations along with the production of higher olefins (C_{4+}; GC), while methylated benzenium ions and alkylated cyclopentenyl species are identified in the three dimensional 10-membered ring channels system of ZSM-5 and in SSZ-13, featuring small 8-membered ring pores and large cages. In the last two cases only the former species, which grows following the S-shaped kinetics typical of MTO, quantitatively correlates with short olefins formation. The presented method applied to the MTO process provides a desirable perspective on the evolution of hydrocarbon species residing in zeolite micropores and those produced during the first stage of the reaction. It also clarifies the topology-dependent relationship between nature of active sites and selectivity that could help to control product selectivity.

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The role of MnO_x and alkali metals in MnO_x-M(Na, K, Rb, or Cs)$_2WO_4/SiO_2$ for product formation in oxidative coupling of methane

A. Zanina[1], V. A. Kondratenko[1], H. Lund[1], E.V. Kondratenko[1*]

[1]*Leibniz-Institut für Katalyse e. V., Albert-Einstein-Str. 29a, 18059 Rostock, Germany*
[*]*evgenii.kondratenko@catalysis.de*

Keywords: oxidative coupling of methane, in situ characterization, active sites, alkali metals

Introduction. MnO_x-Na_2WO_4/SiO_2 is one of the best-performing catalysts in the oxidative coupling of methane (OCM) to C_2H_6/C_2H_4 (C_2-HC). Despite numerous studies with this system, many fundamental aspects (mechanism, active sites, oxygen species, etc.) remain poorly understood. Against this background, we combined in situ catalyst characterization with sophisticated kinetic analysis including surface intermediates to clarify the roles of alkali metal (AM) (M=Na, K, Rb, or Cs) and MnO_x in bimetallic (M_2WO_4/SiO_2) and trimetallic (MnO_x-M_2WO_4/SiO_2) catalysts and to determine the kind of oxygen species involved in selective and unselective pathways.

Experimental/methodology. (MnO_x)-M_2WO_4/SiO_2 catalysts were prepared via an incipient impregnation method and characterized by various techniques including in situ XRD analysis and in situ UV-vis spectroscopy. Steady-state catalytic tests were performed at different degrees of CH_4 conversion. They were complemented by steady-state isotopic transient kinetic analysis (SSITKA), temperature-programmed oxygen isotopic exchange, and temporal analysis of products.

Results and discussion. The catalytic tests with M(Na, K, Rb, or Cs)$_2WO_4/SiO_2$ with or without MnO_x showed that high selectivity to the desired (C_2H_6/C_2H_4) products can be achieved over any catalyst, regardless of the kind of alkali metal and the presence of MnO_x. The Mn-containing catalysts revealed higher rates of CH_4 conversion than the Mn-free catalysts. The activity of the former did not obviously depend on the kind of AM, while an effect was established for M_2WO_4/SiO_2. CH_4 pulse experiments with and without oxygen demonstrated that lattice oxygen of M_2WO_4/SiO_2 is not capable of CH_4 conversion into C_2-HC. In contrast, these products were formed over MnO_x-M_2WO_4/SiO_2. For both systems, the activity is enhanced in the presence of adsorbed oxygen species formed from gas-phase O_2. Importantly, monoatomic and diatomic adsorbed oxygen species were concluded to contribute to the formation of C_2-HC and CO_2, respectively. The ability of M_2WO_4/SiO_2 to generate adsorbed species is affected by the electronic properties of AM [1].

Figure SEQ Figure * ARABIC 1. Transient responses of $H_2{}^{18}O$ (a) and $C^{16}O^{18}O+C^{18}O_2$ (b) over MnO_x-(Na, K)$_2WO_4/SiO_2$.

SSITKA experiments were instrumental to understand the origin of the enhancing effect of MnO_x on the overall catalyst activity (Figure 1). The presence of MnO_x does not result in higher number of active sites/species but increases their reactivity in comparison with MnO_x-free catalysts. Moreover, it was shown that the formation of water is slower than the formation of carbon dioxide. This result suggests that the rate-limiting step can be not the abstraction of C-H bond but the regeneration of catalytically active sites through water formation.

In conclusion, involvement of adsorbed oxygen species in C_2 formation was found to be essential for M_2WO_4/SiO_2. Efficiency of oxygen activation depends on electronic properties of alkali metals. While the participation of both lattice and adsorbed oxygen (Langmuir-Hinshelwood and Mars-van Krevelen mechanisms) was determined for MnO_x-M_2WO_4/SiO_2. According to the SSITKA results, MnO_x has the role of a promoter. No substantial effect of an alkali metal in the trimetallic composition could be confirmed.

Acknowledgments

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Characterization of Zeolite Supported Molybdenum Oxide Nanostructures During Activation for Methane Dehydroaromatization using *Operando* X-ray Absorption Spectroscopy

Noel Joy,[1], Joshua D. Howe[2], Fatemeh Molajafari[2], Rachita Rana[3], Adam S. Hoffman[4*], Ambarish Kulkarni[3], Simon R. Bare[4], Sheima Khatib[1]

[1] *Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA*
[2] *Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, USA*
[3] *Department of Chemical Engineering, University of California, Davis, CA 95616, USA*
[4] *SSRL, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA*
[*] *ashoff@slac.stanford.edu*

Introduction. Molybdenum supported in zeolite H-ZSM-5 (Mo/HZSM-5) is one of the most effective catalysts for direct conversion of methane to aromatics through methane dehydroaromatization (MDA). The initial steps of the MDA reaction take a Mo-oxo species and form carbidic- and oxycarbidic-Mo in the presence of methane. While it is agreed that the Mo starts as an oxide, there is debate in the literature as to what is the nature or structure of the Mo-oxo species prior to exposure to methane.[1-2] In this work we used temperature programmed oxidation (TPO) and *operando* X-ray absorption spectroscopy (XAS) combined with DFT and advanced modeling to characterize how synthesis methods lead to different Mo-oxo species.

Experimental/methodology. Mo/HZSM-5 samples were synthesized with varying Mo loadings through physical mixing of MoO_3 and H-ZSM-5 or through incipient wetness impregnation of H-ZSM-5 with ammonium heptamolybdate tetrahydrate. Operando XAS spectra at the Mo K-edge (20,000.0 eV) were recorded at the Stanford Synchrotron Radiation Lightsource as samples were treated under flowing air up to 700°C with effluent gas measured by mass spectrometry. XAS correlation and deconvolution methods and DFT combined with XAS modeling were used to identify the evolution of Mo species.

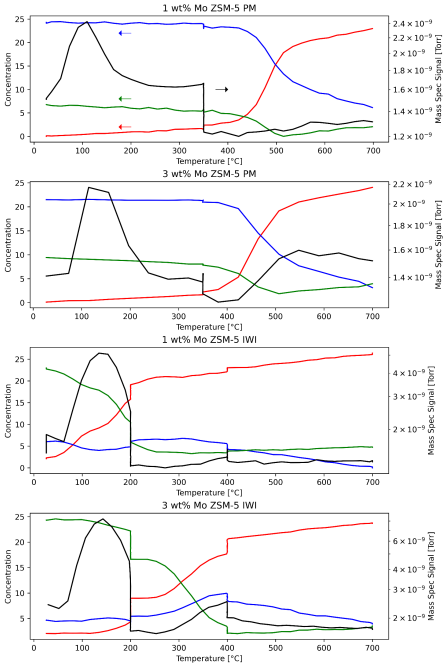

Figure 1. Water (m/z = 18) signal in the mass spectrometer and the concentration of each XAS MCR-ALS score as a function of temperature during TPO.

Results and discussion. *Operando* XAS was used to track the Mo speciation during the TPO. Principal component analysis (PCA) and multivariate curve resolution-alternating least squares (MCR-ALS) analysis on the XAS spectra during the TPO were used to identify the evolution of species. When correlated[3] to the water signal in the mass spectrometer and sample temperature it was shown that the formation of the anchored Mo-oxo species predominantly occurs during dehydration of the IWI samples while formation of the Mo-oxo species occurs at much higher temperatures for the physically mixed samples. DFT simulations combined with QuantEXAFS[4] analyzing the extended X-ray absorption fine structure (EXAFS) spectra of the activated Mo species post-TPO show that mono- and dimeric Mo-oxo species are formed during the TPO. Moreover, these species are dependent and tunable based upon the choice of Mo precursor, synthesis method, Mo loading, and zeolite acidity.

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Enhancing the performance of Co-Ru supported on CeO_2 for the dry reforming of methane via a mechanochemical process

M. Armengol-Profitós[1], I. J. Villar-Garcia[2], V. Pérez-Dieste[2], C. Escudero[2], N. J. Divins[1*], J. Llorca[1*]

[1]*Institute of Energy Technologies, Department of Chemical Engineering, Universitat Politècnica de Catalunya, EEBE, Barcelona, Spain*

[2] *ALBA Synchroyton Light Source, Cerdanyola del Vallès, Barcelona, Spain*

[*]*E-mail: nuria.jimenez.divins@upc.edu, jordi.llorca@upc.edu*

Keywords: hydrogen production, syngas, NAP-XPS, methane dry reforming, bimetallic catalysts

Introduction. Dry reforming of methane (DRM) is a key method for hydrogen production and a preferred first step in the Fischer-Tropsch synthesis. Despite intensive investigation, limitations and drawbacks still exist, which have to be solved: deactivation due to carbon deposition, low CO_2 activation, and compatibility with a green feedstock as biomethane [1]. When creating an active and stable catalyst, the activation of the reactants (CH_4 and CO_2) is a major consideration. The incorporation of ruthenium in a Co/CeO_2 catalyst [2] by a mechanochemical synthesis is investigated to enhance the performance of the monometallic catalyst.

Experimental/methodology. Mono- and bimetallic samples are synthesized by conventional impregnation method (IWI) and ball milling (BM). All catalysts were tested from 550 to 950 ⏭C. Operando synchrotron X-ray diffraction (SXRD) and Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) techniques were used to comprehend the interaction between the two metals and with the support.

Results and discussion. Higher CH_4 and CO_2 conversion were obtained by the mechanochemically-prepared samples (mono- and bimetallic), outperforming their conventionally synthesized counterparts. SXRD results suggest the inclusion of cobalt in the structure of the RuO_2 due to a shift in the peaks of the bimetallic as-prepared samples, as well as the stabilization of smaller metal nanoparticles in the bimetallic IWI sample. NAP-XPS results show that Ru addition alters the metal-support interaction with higher Ce^{3+}/Ce ratios for the bimetallic samples and modifies the oxidation state of Ru. In addition, the synthesis method revealed an impact on the species' reducibility and rearrangement during the DRM reaction, as shown in Fig. 1. Cobalt species under DRM conditions at 550 ⏭C exhibited different oxidation states, with the BM catalysts being more oxidized at lower temperatures due to a stronger ability to activate CO_2. In the high-temperature regime (700 ⏭C), the BM catalysts had a greater reduction degree than their IWI counterparts, most likely as a result of a higher methane conversion rate. These findings demonstrated that the surface of the milled catalyst is more reactive and dynamic than their conventionally-impregnated equivalents.

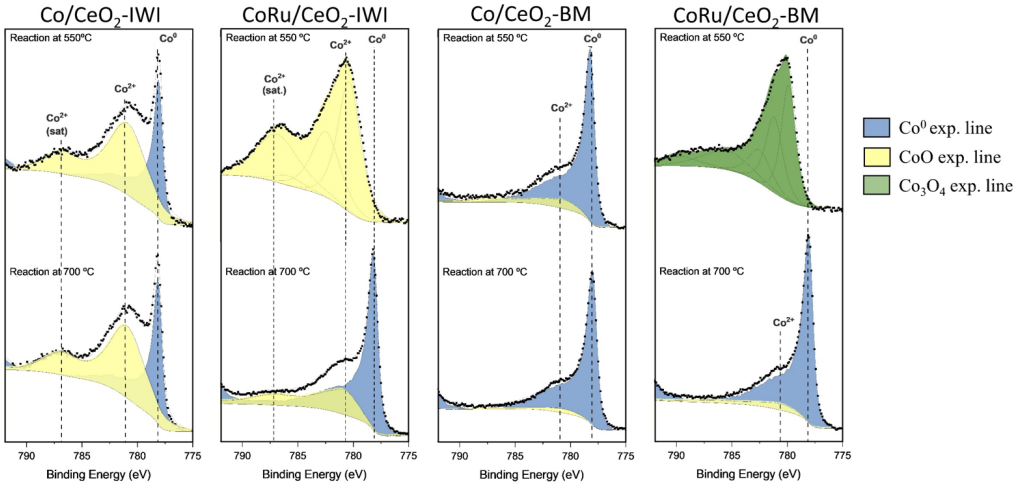

Fig. 1. NAP-XPS spectra of the Co 2p region of Co/CeO_2 and $CoRu/CeO_2$ catalysts, IWI and BM under CH_4+CO_2 at 1 mbar at 550 and 700 °C, scans obtained with a KE of 215 eV.

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Ru-REO/Al_2O_3 as dual-functional materials for combined CO_2 capture and methanation: An operando DRIFTS study

Lizbeth Moreno Bravo[1], Frederic Meunier[2], and Jan Kopyscinski[1*]

[1]*Department of Chemical Engineering, McGill University, Montreal, Canada*
[2]*Université Claude Bernard Lyon, CNRS, IRCELYON, Villeurbanne, France*
**jan.kopyscinski@mcgill.ca*

Introduction. In recent years, some studies have focused on combining CO_2 capture and subsequent methanation in the same reactor by using Dual-Functional Materials (DFMs) [1-2]. DFMs contain sorbent (mostly alkali metal oxides) and catalyst (Ni, Ru) components. This combination enables selective CO_2 capture from a gas stream to later hydrogenate the adsorbed CO_2 to CH_4 via isothermal cyclic operations. We propose rare-earth metal oxides (REO) as sorbents due to their higher surface basicity, yielding additional CO_2 adsorption sites [3] and the highly active Ru as hydrogenation site. To gain a better understanding of the reaction mechanism (CO_2 uptake, hydrogenation), the involved surface intermediates, and the structure-reactivity/selectivity relationship of the catalysts, we conducted operando diffuse reflectance infrared spectroscopy (DRIFTS) analyses to determine the CO_2 storage capacity and CH_4 yield.

Experimental/Methodology. A series of Ru-REO/Al_2O_3 catalysts were synthesized via incipient wetness impregnation on commercial alumina. First, REO (10 wt% of Gd_2O_3, Sm_2O_3, Nd_2O_3, Ce_2O_3) was impregnated on the alumina support and calcined at 700 °C. Then, ruthenium (5 wt%) was added and calcined at 350 °C. Prior to activity testing, catalysts were reduced under 20% vol H_2/Ar. CO_2 uptake and methanation experiments were conducted in a fixed-bed reactor, TGA, and DRIFTS reactor at 200-500 °C and 1 bar_{abs} at various flow rates and partial pressures. Product gas was analyzed via mass-spectrometry (MS) and/or IR spectroscopy. The morphology, crystallinity, and textural properties of the catalysts were investigated by means of N_2 adsorption/desorption, H_2 chemisorption, XRD, SEM-EDS, TEM. Long-term cycling experiments were also performed using TGA-MS to test material stability.

Results and discussion. Under methanation conditions, all Ru-REO/Al catalysts exhibited high CH_4 selectivity (>97 %), specially at low temperatures (200-250 °C) where almost no CO formation was observed. The addition of different REOs improved catalytic activity and increased CH_4 production up to 30%, with RuSm/Al performing best. In all cases, the hydrogenation pathway only existed on Ru, as proved by DRIFTS. Upon CO_2 exposure during the cycled experiments, higher formation of hydrogen-carbonates, mono- and bidentate carbonates occured on the surface of Ru-REO/Al catalyst in comparison to Ru/Al. These species contribute to additional promoter-related pathways in parallel to the Ru-based pathway. Fig. 1 presents the DRIFT results for one cycle of CO_2 capture (red spectra) and subsequent hydrogenation (blue spectra) with He flush steps (green spectra) in between. In this sample, after CO_2 saturation, the Ru-CO (2019 cm^{-1}) bond remains stable under He, but is rapidly hydrogenated upon H_2 introduction. Formates and carbonates (1321-1643 cm^{-1}) show a mix of fast and slow reaction rates, hinting at the presence of both weakly and strongly bound species, as well as spectator species. After the hydrogenation step (under He atmosphere), a carbonate's spillover to Ru active sites is observed (~2000 cm^{-1}, top green spectra), which can be hydro-genated to CH_4. This process is slow and does not significantly contribute to overall conversion. Preliminary characterization results indicate that REO addition: (1) increases CO_2 uptake, while lowering H_2 uptake; (2) N_2 physisorption shows no significant surface area loss; (3) CO_2-TPD highlights that the overall basicity of the material was increased, creating favorable metal–support interactions that yield higher catalytic activity for CO_2 capture and hydrogenation.

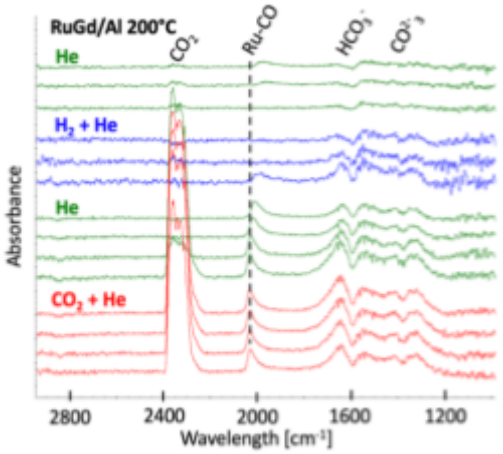

Fig. 1 Isothermal DRIFTs for $RuGd_2O_3$/ Al_2O_3 at 200 C under different gas conditions.

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Detecting Surface Intermediates Beyond Carbon Monoxide in the Copper-Catalyzed Electroreduction of Carbon Dioxide

J. de Ruiter*, B. den Hartigh, W. van der Stam, B.M. Weckhuysen
Inorganic Chemistry and Catalysis, Institute for Sustainable and Circular Chemistry and Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, Netherlands
*J.deruiter@uu.nl

Introduction

The electrochemical reduction of CO_2 (eCO2RR) on copper has gained increasing attention as it has the potential to store intermittent renewable energy in chemical bonds. Copper has the unique ability to catalyze the formation of C-C bonds (*e.g.*, ethylene) in eCO2RR, but the behavior of reaction intermediates at the copper surface remains debated. [1,2] Experimentally it has been observed that residual oxides boost the C-C coupling efficiency. In order to understand the beneficial influence of oxygen on the surface, *in situ* Raman spectroscopy has proven to be a great tool to probe the copper surface during the eCO2RR process.[3] Although *in situ* Raman spectroscopy measurements have shown that linear adsorbed CO is one of the main intermediates on oxide-derived copper surfaces, many other observed Raman signals are still not confidently assigned to specific surface species.[3]

Results and discussion

Here, we present a systematic approach to gain more insights in the different surface species on oxide-derived copper electrocatalysts. These surface species are characterized by strong vibrational features in the low wavenumber region (around 500 cm^{-1}), indicating metal-adsorbate vibrations. By studying the behavior of these intermediates as function of both potential and time, it was observed that initially after the reduction of Cu_2O, linear CO vibrations dominate the copper surface ($\delta_{Cu\text{-}CO}$ 280 cm^{-1}, $\nu_{Cu\text{-}C}$ 360 cm^{-1}, and ν_{CO} 2090 cm^{-1}). However, after 15 min these linear CO vibrations fade out, whereas the vibrational features around 500 cm^{-1} grow in intensity, as shown in Figure 1a below. These surface intermediates are related to Cu-C intermediates, as evidenced by isotope labeling, and more strongly bound to the copper surface, as indicated by the increased vibrational energy ($\nu_{Cu\text{-}C}$ 500 cm^{-1} vs. ν_{CuC} 360 cm^{-1}). It is observed that the surface (composition and coverage) can be tuned by the introduction of anodic pulses, which regenerate the copper oxide catalyst and reintroduce Cu-CO at the surface, as observed in Figure 1b. This observation suggests that the 500 cm^{-1} bands correspond to intermediates beyond CO.

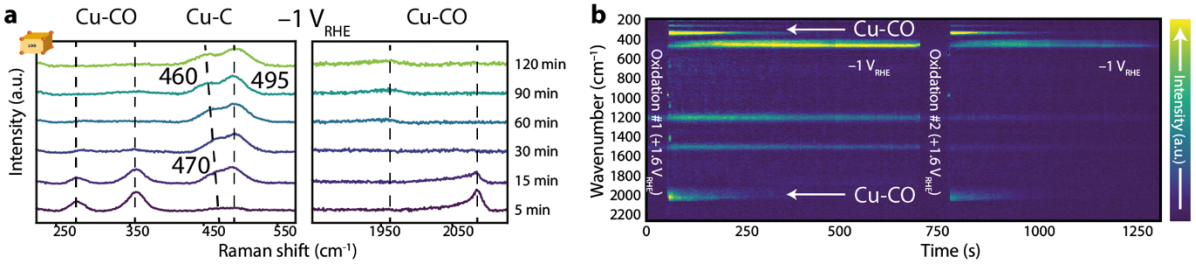

Figure 1 – a) Time dependent Raman spectra during eCO2RR on Cu_2O cubes at –1 V_{RHE}. b) Heatmap of Raman spectra before and after anodization, showing a rich CO coverage directly after surface oxidation.

Acknowledgments

This work was supported by the Strategic Alliance between Utrecht University, University Medical Center Utrecht and Technical University Eindhoven. B.M.W. acknowledges funding from the Netherlands Center for Multiscale Catalytic Energy Conversion (MCEC), an NWO Gravitation program funded by the Ministry of Education, Culture, and Science of the government of the Netherlands.

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Insights on Au nanoparticle dynamics by UV-Vis *operando* spectroscopy: an application to CO_2 activation *via* reverse water gas shift

C. Negri[1], R. Colombo[1], C. Atzori[2], A. Donazzi[1], A. Lucotti[3], M. Tommasini[3], M. Maestri[1*]

[1] *Laboratory of Catalysis and Catalytic Processes, Department of Energy, Politecnico di Milano, Milano, Italy*

[2] *European Synchrotron Radiation Facility, Grenoble, France*

[3] *Department of Chemistry, Materials and Chemical Engineering, Politecnico di Milano, Milano, Italy*

[*] *matteo.maestri@polimi.it*

Keywords: CO_2 activation, Gold nanoparticles, RWGS, Surface Plasmon Resonance, UV-Vis spectroscopy

Introduction. A key-challenge in reaction engineering is the constant demand for more efficient catalysts and sustainable processes, which requires a deep knowledge of the catalyst functionality at atomistic level.[1] In this scenario, we focused on studying gold nanoparticles that, when highly dispersed on a support, are active for CO_2 hydrogenation by means of renewable H_2 *via* reverse water gas shift (*r*WGS) reaction ($CO_2 + H_2 \rightleftarrows CO + H_2O$).[2] To study their changes in size and shape as a function of the reaction feed, we exploited the surface plasmon resonance (SPR) phenomenon,[2c,d] which intrinsically depends on the nanoparticle structure, as a fingerprint for the *operando* characterization of the active nanoparticles.

Experimental/methodology. A 4%Au/α-Al_2O_3 catalysts was tested in an *ad-hoc* optimized *operando* UV-Vis setup, with a quartz reactor connected to a microGC. The *operando* UV−Vis experiments were performed during the reduction pretreatment (from RT to 200°C, 2°C/min, 50 Ncc/min−5% H_2/N_2 balanced) and during the *r*WGS catalytic testing (50 Ncc/min, CO_2/H_2=1, GHSV=15000 h^{-1}). The reaction was monitored over time, until steady state was reached both in the spectra and in CO_2 conversion. Measurements were carried out from RT to 600 °C with a heating ramp of 5°C/min, flowing the desired gases (H_2/N_2 or $CO_2/H_2/N_2$) with an *ad hoc* built gas flow setup. *Operando* XAS and PXRD data were collected at BM31 beamline [3] of the European Synchrotron Radiation Facility.

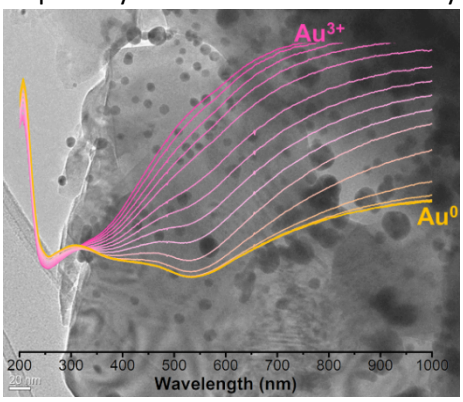

Figure 1. *Operando* diffuse reflectance UV-Vis spectra of Au/α-Al_2O_3 reduction in 5% H_2/N_2 flow, from RT to 200°C (pink to gold curves) and HRTEM image of gold NPs formed during the reduction ramp.

Results and discussion. In this contribution surface plasmon resonance (SPR) is proposed for the first time to monitor metal nanoparticles morphology in condition relevant for the catalysis. UV-Vis *operando* spectroscopy allowed us following the dynamics of nanoparticles formation and their subsequent reactivity during reverse water gas shift reaction. We monitored the progressive change in coordination of Au^{3+} ions, and the behaviour of the formed gold nanoparticles in reaction conditions, through the the SPR peak. Namely, the SPR peak position of supported gold nanoparticles was found to be affected both by the nanoparticle dimensions and the presence of agglomerates. The catalytic results measured during the *operando* UV-Vis experiment evidenced a good activity for *r*WGS of the Au catalyst, with a 100% CO selectivity. *Operando* XAS and PXRD data confirmed the experimental evidences from UV-Vis spectroscopy, showing that Au nanoparticles are formed with very small size and are stable in reacting feed. The results obtained proved the potential application of the SPR to the study of catalysts morphology. To our knowledge this approach represents a novelty with respect to literature, allowing for obtaining direct information on the structure-activity relation in the field of metal-based supported catalysts.

Acknowledgments

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Cu-bipy complexes for light hydrocarbon oxygenation reactions

G. Deplano[1], B. Centrella[1], M. Signorile[1], M. Bonomo[1], S. Jannuzzi*[2], A. Damin[1], C. Barolo[1], S. DeBeer[2], S. Bordiga*[1]

[1] *Department of Chemistry and NIS Interdepartmental Center and INSTM reference center, University of Turin, Via Quarello 15A and via Pietro Giuria 7, 10135 and 10135 Torino, Italy*
[2] *Department of Inorganic Spectroscopy, Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34–36, 45470 Mülheim an der Ruhr, Germany*
*silvia.bordiga@unito.it, sergio.jannuzzi@cec.mpg.de

Keywords: Cu-complexes, hydrocarbon oxidation, *in situ* spectroscopy, UV-Vis, EPR, DFT, modeling

Introduction. The selective oxidation of hydrocarbons is an important class of reactions for environmentally conscious resource management in chemistry. Oxygenated analogues often improve transport and stocking options, and many of these relatively simple molecules are in high demand as base or platform chemicals. The current way of performing these reactions on a large scale often involves the use of precious metals and/or harsh conditions, and much focus is being put in the development of milder alternatives. In this context, Cu-based catalysts are studied as simple redox systems that can carry out this reactivity in both heterogeneous (zeolites, MOFs) and homogeneous (complexes, enzymes) phases. Understanding the reaction mechanism, structure-activity relationships and catalyst deactivation pathways is crucial for rational catalyst design, and a wide variety of spectroscopic techniques and theoretical tools are available for this task. In this work, we propose $[Cu(6,6'\text{-dimethyl-}2,2'\text{-bipyridyl})_2]PF_6$ as a catalyst in solution for the oxidation of cyclohexene into 2-cyclohexen-1-one and 2-cyclohexen-1-ol using *tert*-butyl hydroperoxide (tBuOOH). The Cu(I)/Cu(II) redox cycle involved in this reaction is studied via time-resolved *in situ* UV-Vis and EPR spectroscopies, aided by multivariate curve resolution (MCR) modeling and density functional theory (DFT) calculations. The results indicate the formation of an oxygenated species on the complex as fifth ligand and the involvement of this adduct as the key intermediate for this reaction.

Experimental/methodology. UV-Vis-NIR spectra have been recorded on an Agilent 8454 spectrophotometer on a 0.2 cm cuvette and on a 1.0 cm cuvette with a 40 ml reservoir and septum stopper. Sample aliquotes were extracted with a syringe after each UV-Vis spectrum and frozen for EPR analysis on a Bruker X-band Elexsys spectrophotometer. All DFT calculations were carried out using the ORCA software (version 5.0.3).

Results and discussion. As suggested by previous results [1], the conversion of the substrate towards the products is mediated by an oxidized form of the complex that presents an additional O-containing ligand. Time-resolved *in situ* UV-Vis and EPR spectra (**Figure 1**) confirm the presence of at least two interconverting Cu(II) species that start forming after the addition of tBuOOH. DFT simulation of UV-Vis spectra for possible candidates, as well as g- and A-values extracted from EPR fitting, are consistent with a 5-coordinated species with a strained geometry for the final state. Additionally, the MCR extraction of pure spectra and concentration profiles allows to disentangle the UV-Vis spectra of the two Cu(II) species and to trace a kinetic profile of the reaction that agrees well with the catalytic tests. The combination of these spectroscopic and modeling tools is able to extract crucial information on the intermediates, and will be applied to study the second half of the catalytic cycle (i.e., the oxygenation of cyclohexene) to shed light on the key mechanistic aspects of this reaction.

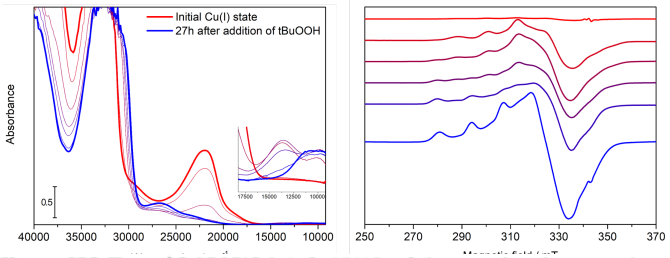

Figure SEQ Figure * ARABIC 1. Left: UV-Vis of the complex along reaction with tBuOOH (inset: zoom on the d-d transition zone). Right: EPR spectra of the same reaction.

Acknowledgments
This work was supported by the European Research Council (ERC), under the Horizon 2020 research and innovation program: CuBE ERC-Synergy project (Grant agreement n° 856446).
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Following the evolution of PdZn nanoparticles used for CO_2 activation

Sofia Mediavilla Madrigal[1,2*], Andrew M. Beale[2,3], Naomi Lawes[1] and Stephen Parry[4]

[1]*Cardiff Catalysis Institute, School of Chemistry, Cardiff University, UK*
[2]*UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, UK*
[3]*Department of Chemistry, University College London, UK*
[4]*Diamond Light Source Ltd, Harwell Science and Innovation Campus, UK*
[*]*mediavillamadrigals@cardiff.ac.uk*

Keywords: CO_2 conversion, catalysis, spectroscopy, X-rays

Introduction. Converting CO_2 into value-added products has seen renewed interest due to the considerable increment in emissions into the atmosphere. Utilising it to synthesise liquid fuels like methanol would reduce the dependence on fossil fuels as the primary energy feedstock. Although methanol is already produced on a global scale using copper-based catalysts (i.e., $Cu/ZnO/Al_2O_3$) operating at high pressure (> 50 bar gas), recent focus is on novel processes able to use more (hydrothermally) stable catalysts capable of producing methanol at lower pressures and temperatures (and thus with lower energy costs). One of the most promising catalyst design concerns supported PdZn nanoparticles, e.g., $PdZn/TiO_2$ catalysts [1]. Combined *operando* XAFS-XRD studies were conducted to gain insights into how structural changes affect the activity of these catalysts under reaction conditions while varying the Zn concentration and to study the salient properties and formation of the β-PdZn 1:1 alloy.

Experimental/methodology. $PdZn/TiO_2$ catalysts with varying Pd:Zn ratios and 5 wt% Pd fixed loading were prepared by chemical vapour impregnation. Combined XAFS-XRD studies at Pd and Zn K-edge were conducted at the B18 beamline at Diamond Light Source. Before testing, the catalysts were reduced *in situ* in a flow of 4 % H_2/Ar gas at 400 °C for 1h. Catalytic tests were performed at 250-270 °C and 20 bar under a gas flow of 1:3 CO_2:H_2 molar ratio. The effluent gases of the reactor were analysed by mass spectrometry.

Results and discussion. Catalytic testing prior to beamtime experiments showed that tailoring the Pd:Zn allowed us to control the methanol yield. However, the underpinning reason(s) why were unknown. In all cases, the β-PdZn 1:1 alloy was observed to form in the XRD data after reduction and appeared to be necessary for optimal activity. However, at high Pd:Zn ratios, there was some evidence of metallic Pd presence, possibly as part of a core-shell structure of the otherwise PdZn particles, influencing catalytic activity. However, at this point, the exact nature and structure of the active nanoparticles in these formulations are unclear [2, 3].

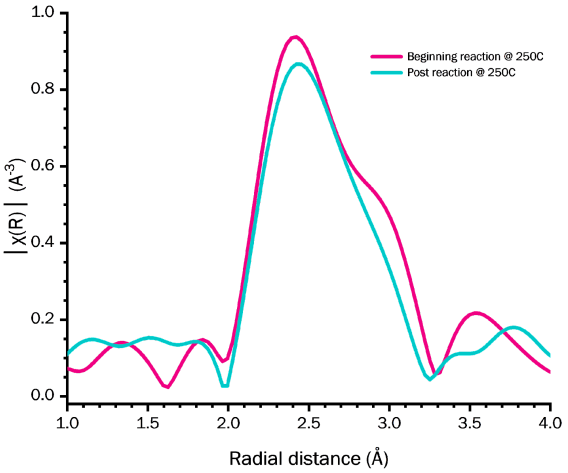

Figure 1. Changes in the Phase-corrected Fourier transform representation of Pd K-edge k^2-weighted EXAFS spectra observed during reaction conditions on PdZn/TiO$_2$.

When subjecting the same samples to the reaction gas mixture, a change was observed in the Pd-edge k-space of $PdZn(1:20)/TiO_2$, where the intensity of the oscillations diminished, corresponding to the disappearance of a shoulder ca. 2.8 Å in the Fourier transform representation (Figure 1), implying that the PdZn alloy phase, and/or its surrounding neighbours had evolved under reaction conditions. These results, together with changes seen in the MS signal simultaneously, demonstrate that small differences in the structure and composition of supported nanoparticles play a key role in the catalytic properties, and testing under more realistic conditions is very valuable, as has already been shown for Cu/ZnO-based catalysts [4].

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Catalytic behaviour and surface changes of MAX phases and MXenes

Alexandra C. Iacoban[1,2*], Toton Haldar[1], Florentina Neatu[1], Stefan Neatu[1], Luca Artiglia[3], Michel Barsoum[4], Mihaela Florea[1]

[1]*National Institute of Materials Physics, 405A Atomistilor Street, 077125 Magurele, Romania*
[2]*Interdisciplinary School of Doctoral Studies, University of Bucharest, Mihai Kogalniceanu, 36-46, 050067 Bucharest, Romania*
[3]*Paul Scherrer Institut, CH-5232 Villigen-PSI, Switzerland*
[4]*Department of Material Science and Engineering, Drexel University, Philadelphia, USA*
[*]*alexandra.iacoban@infim.ro*

Introduction. Layered ternary carbides structures, such as in MAX phases (3D) are remarkable materials that combine the properties of metals and ceramics. They have the general formula $M_{n+1}AX_n$, where M is an early transition metal, A is a group A element, X= C and/or N, with n=1-4 [1]. These materials have important properties such as high thermal and electrical conductivity, mechanical strength, low density, and also resistance to high temperatures and oxidation [2,3]. By selectively etching, 2D MXene are obtained that exhibit quite different electronic, magnetic, optical, and electrochemical properties. Moreover, they present abundance of hydrophilic functional groups on the surface (-OH, –O and –F) formed during wet-etching synthesis of MXenes from MAX phases, implying promising (photo)catalytic properties [4]. However, little is understood about the dynamics of the structural and surface changes that these systems go through during catalysis that result in efficient catalyst function.

Experimental/methodology. Several materials, including MAX phase (Ti_3SiC_2) and MXene ($Ti_3C_2T_x$) were studied at the X07DB-In Situ Spectroscopy beamline at the Swiss Light Source Synchrotron. The dynamics of the surface and subsurface rearrangements were investigated under steady state Ar, O_2, CH_4 and/ or H_2O environment at different temperatures (between room temperature and 350 ˚C) and ambiental pressure. Thus, the effects of reduction and oxidation conditions were evaluated. Sensitive surface and subsurface in situ XPS spectra were obtained at different kinetic photoelectron energies (300 and 600 eV). Furthermore, materials were characterized before and after the reaction with the help of different experimental techniques, such as XRD, TEM, UV-Vis and Raman spectroscopies.

Results and discussion. The dynamics of the structural and surface changes were studied at 1 mbar, under Ar, CH_4+ O_2 and CH_4+ O_2+ H_2O. The most significant result of this work was the presence of OH surface species on the MXene surface when CH_4 was present, which might be due to the activation of CH_4 on the metal species, then one C–H bond is broken and the resulting H is immediately attached to the O species on the surface. In addition, a good stability of the of MAX phase and MXene throughout the AP-XPS experiments was confirmed. The obtained results are of great interest in undertanding the behaviour of MAX phase and MXene in catalytic processes.

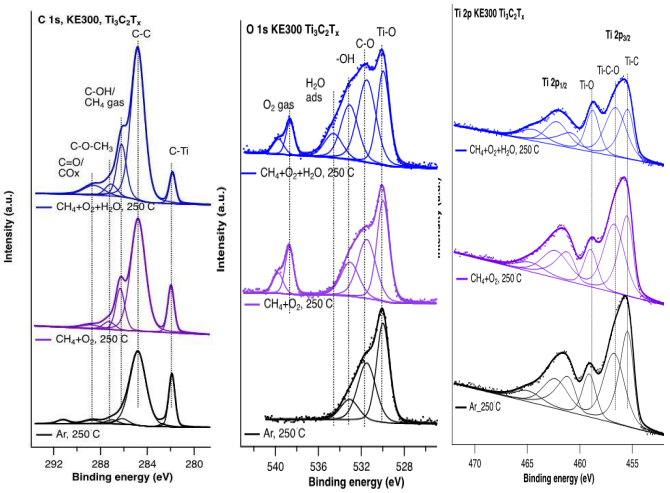

Figure SEQ Figure * ARABIC 1. XPS spectra for C1s, O1s and Ti2p at 300 eV

Acknowledgments

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Bimetallic Pd-based catalysts for selective hydrogenation of butadiene

O.E. Brandt Corstius[1*], H.L. Nolten[1], Z. Xu[2], E.J. Doskocil[2],
J.E.S van der Hoeven[1], S.T. Roberts[3], G.S. Sunley[3], P.E. de Jongh[1]

[1]*Materials Chemistry and Catalysis, Utrecht University, Utrecht, The Netherlands*
[2]*Applied Sciences, bp Innovation and Engineering, Chicago, IL, United States*
[3]*Applied Sciences, bp Innovation and Engineering, Hull, United Kingdom*
[*] *o.e.brandtcorstius@uu.nl*

Keywords: Selective hydrogenation, Butadiene, Pd-based catalysts, Bimetallic, Promoter, Synergy

Introduction. The catalytic performance of bimetallic nanoparticles critically depends on the atomic distribution of the metals within the particles.[1,2] Monometallic Pd and Cu have excellent activity and selectivity in (selective) hydrogenation reactions, respectively.[2,3] Interestingly, synergistic catalytic performance can be achieved in bimetallic CuPd systems, due to both geometric and electronic effects.[4,5]

Experimental/methodology. Bimetallic CuPd nanoparticles with molar Cu:Pd ratios varying from 7:1 to 167:1 were prepared by colloidal approach. In short, Cu(I)- and Pd(II)acetate was heated in trioctylamine and tetradecylphosponic acid which resulted in particles of 7±1 nm in size. Heterogeneous CuPd/C catalysts were prepared by a wet impregnation of the colloidal suspension onto carbon support, followed by drying and calcination. After reduction, their catalytic performance was tested in the selective hydrogenation of 0.3% 1,3-butadiene from a 30% propylene feedstock in 20% hydrogen (He as balance).

Results and discussion. Extensive characterization comprising XRD, STEM-EDX and TPR indicated the co-existence of both metals within individual nanoparticles in all as-synthesized catalysts. EXAFS showed that after reduction (250 °C, H_2), Pd was coordinated mainly to Cu, and to a lesser extent to Pd for the 7:1, 13:1 and 31:1 ratios. The catalysts were active in selective hydrogenation, especially at lower Cu-fraction, with a maximum activity around 31:1 Cu:Pd ratio (Figure 1). Interestingly, limited alkane formation resulted in an optimum in selectivity at similar Cu:Pd ratio. Insight into the origin of the fraction-dependent performance with respect to electronic or geometric effects, and to atomic redistribution during catalysis is under investigation and will be discussed during the conference.

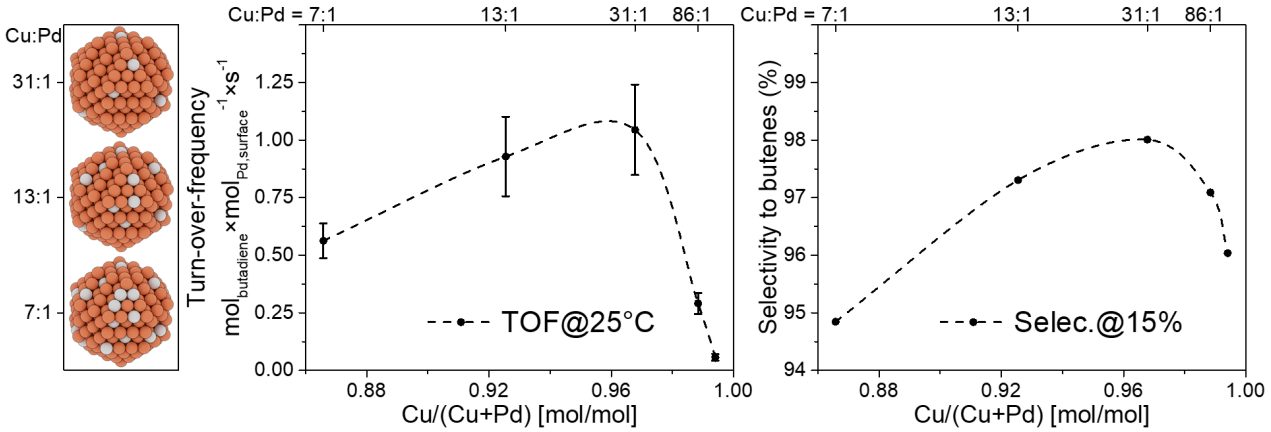

Figure 1. (Left) Schematic representation of bimetallic nanoparticles with varying Cu:Pd ratio. (Middle) Butadiene activity and (right) butene selectivity during selective hydrogenation of butadiene as function of Cu-fraction.

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Origin of active sites on silica–magnesia catalysts in the one-step ethanol-to-butadiene Lebedev process

S. Chung[1], T. Li[1], T. Shoinkhorova[1], S. Komaty[1], A. Ramirez[1], I. Mukhambetov[1], E. Abou–Hamad[2], G. Shterk[1], S. Telalovic[1], A. Dikhtiarenko[1], P. Lavrik[1], X. Tang[2], J. Gascon[1], and J. Ruiz–Martinez[1*]

[1]*King Abdullah University of Science and Technology, KAUST Catalysis Center, Thuwal 23955, Saudi Arabia*
[2]*King Abdullah University of Science and Technology, Core Labs, Thuwal 23955, Saudi Arabia*
[*]*e-mail: sangho.chung@kaust.edu.sa, javier.ruizmartinez@kaust.edu.sa*

Introduction. Wet-kneaded silica–magnesia is a benchmark catalyst for the one–step ethanol-to-butadiene Lebedev process [1-3]. Magnesium silicates, formed during wet-kneading, have been proposed as active sites responsible for butadiene formation, and their catalytic performance has been mainly explained by the variations in the ratio of acid and base sites. While the Lebedev process was developed in the 1930s, a detailed insight into how the peculiar, yet essential wet-kneading synthesis leads to the generation, location, and catalytic role of magnesium silicates has not been fully established [3].

Experimental/methodology. Typically, we prepared the conventional wet-kneaded silica-magnesia catalysts using Stöber silica and platelet shaped $Mg(OH)_2$ [1,2]. For the modified wet-kneading, the pH of the aqueous wet-kneading medium was adjusted, yielding two model catalysts [1]. The prepared catalysts were characterized by ICP-OES, SEM, TGA, PXRD, N_2 and Ar physisorption, NH_3- and CO_2-TPD, DRIFTS-MS, solid-state ^{29}Si and ^{25}Mg NMR. The catalytic activity of the samples were tested using high-throughput reactor system (Avantium) at 425 °C and ambient pressure (LHSV 1.0 h^{-1}).

Results and discussion. Here, we demonstrate that magnesium silicates formation occurs via dissolution of Si and Mg subunits from SiO_2 and $Mg(OH)_2$ precursors, initiated by the alkaline pH of the aqueous wet-kneading medium, followed by cross-deposition of the dissolved species on the precursor surfaces (Fig. 1a,b). The model catalysts prepared selective dissolution/cross-deposition (Fig. 1c) showed different catalytic roles in the Lebedev process: Si/MgO and Mg/SiO_2 for butadiene and ethylene, respectively (Fig. 1d). The close proximity of acidic and basic sites in Si–OH–Mg species in Si/MgO is thought to be key to efficient conversion [2,3]. To proof that, we have developed a spectroscopic titration approach revealing that the Si modification on MgO (Si/MgO) creates additional acid sites and these sites are indeed in close to basic sites in 5 Å range (Fig. 1e). We also show that the adsorption affinity of acetaldehyde on the catalyst surface has been reduced by surface modification with Si on MgO (Fig.1f).

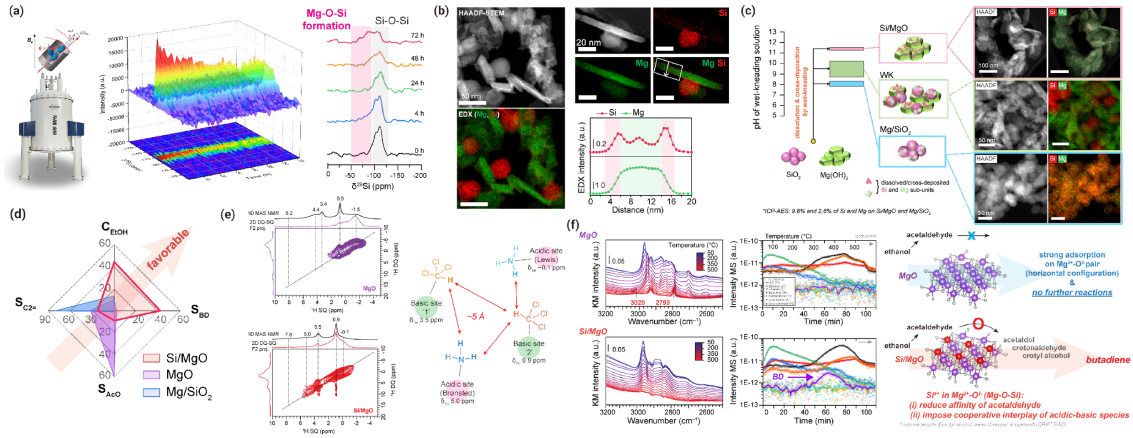

Figure 1. (a) In situ ^{29}Si solid-state NMR during wet-kneading, (b) TEM-EDX results of conventional silica-magnesia, (c) two model catalysts prepared by modified wet-kneading, (d) catalytic activity results, (e) 2D ^{1}H SQ-DQ MAS NMR for acid-base sites proximity, and (f) DRIFT-MS spectra for MgO and Si/MgO.

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Revealing activating and deactivating effects of carboxylic acids on polyoxometalate-catalysed three-phase liquid-liquid-gas reactions using theoretical and analytical tools

M. J. Poller[1], S. Bönisch[2], B. Bertleff[3], J. Raabe[1], A. Görling[2], and J. Albert[1]*

[1] *Institute of Technical and Macromolecular Chemistry, Hamburg University, Bundesstr. 45, 20146 Hamburg, Germany*

[2] *Chair of Theoretical Chemistry, Friedrich-Alexander-University Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany*

[3] *Institute of Chemical Reaction Engineering, Friedrich-Alexander-University Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany*

[*] *Jakob.albert@uni-hamburg.de*

Keywords: Three-phase liquid-liquid-gas reactions, polyoxometalates, density-functional calculations, spectroscopic investigations, catalyst activation/deactivation

Introduction. Three-phase liquid-liquid-gas reactions are often applied to make valuable chemicals from biomass or to efficiently remove contaminants from fuels. Hereby, molecular oxygen is used as a cheap, abundant and eco-friendly oxidant. Typically, the latter is activated by metal catalysts, whereby polyoxometalates (POMs), especially in their heteropolyacid form (HPA), are very efficient due to their combined Bronsted acidity and redox activity. Mostly used in homogeneously catalysed oxidations are HPAs from the so-called Keggin-type $H_{3+n}[XV_nM_{12-n}O_{40}]$ (HPA-x). Hereby, the catalytic activity is mostly introduced by substituting some of the framework metals (tungsten, molybdenum) with easily reducible heterometals like vanadium that results in shifting their reactivity from acidic to redox-dominance. [1]

Experimental/methodology. HPA-5 and HPA-2 were synthesized according to literature-known procedures. [2] All calculations were performed with the Turbomole program package. [3] ATR-FT-IR spectra were measured on a Shimadzu IRSpirit instrument with ATR accessory unit. Raman spectra were recorded in aqueous solution, using a Kaiser Raman Rxn1-785 instrument, equipped with an immersion probe. The excitation laser used a wavelength of 785 nm. NMR spectra were measured by the central NMR service facilities of the Universität Hamburg, using a 600 MHz instrument (242.94 MHz for 31P, 157.77 MHz for ^{51}V). UV-Vis spectra were recorded using a Cary 60 UV-Vis spectrometer (Agilent Technologies) in a 3 mL Quartz cuvette (QS).

Results and discussion. Three-phase liquid-liquid gas reactions are promising strategies to combine highly active and selective homogeneous-catalysed oxidation reactions with in-situ product isolation. Hereby, an aqueous POM catalyst solution in combination with molecular oxygen as oxidant is used. However, contrary effects on the oxidation performance of the POM-catalyst were observed for different carboxylic acids as reaction products or intermediates. By using model calculations employing Density-Functional Theory (DFT) in combination with magnetic and optical spectroscopy, we could explain the experimental observations that oxalic acid activates the POM catalyst and therefore promotes its oxidation performance while acetic and especially formic acid form stable complexes with the active centres and therefore inhibit the oxidation activity. These findings greatly improve the understanding of POM-acid complexes and their effect on the catalytic performance. [4]

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Operando XAS identifies monomeric Fe species in square planar geometry to be the active sites for low temperature NH_3-SCR of NO

D. Wierzbicki[1,2], D. Ferri[1], A.H. Clark[1], O.Kröcher[1], M. Nachtegaal[1*]

[1]*PSI, Villigen-PSI, Switzerland*
[2]*AGH University of Science and Technology, Cracow, Poland*
[*]*maarten.nachtegaal@psi.ch*

Keywords: Fe-ZSM-5, SCR, XAS

Introduction. Fe containing zeolites are active for N_2O decomposition and selective catalytic reduction of NO by NH_3 [1,2]. In the last decades, much effort has been focused on identifying the structure of the most active Fe species, to optimize the method of Fe introduction into zeolites and to clarify the reaction mechanism[3]. The synthesis of Fe/zeolites containing monomeric Fe species, which are suggested to make up the active low temperature species, is challenging as Fe tends to cluster readily. In the current study an Fe-EDTA complex was used as the Fe precursor to ensure separation of iron ions in the ZSM-5 zeolite pores. Such a procedure resulted in synthesis of a Fe catalyst with monomeric Fe, which showed very high activity in the low temperature NH_3-SCR process[4].

Experimental/methodology. A NH_4-ZSM-5 zeolite with MFI structure (SiO_2/Al_2O_3 = 23; 400 m^2/g; Alfa Aesar) was dealuminated using an aqueous solution of HNO_3 (2 M; 100 ml/g of zeolite) at 80°C for 24 h. Subsequently, the material was filtered, washed with distilled water (2 L) and dried at 80°C overnight. The Fe-EDTA was added dropwise to an aqueous suspension of dealuminated ZSM-5 preheated to 65°C under N_2 atmosphere[4]. *Operando* Fe K-edge XAS studies were carried out at the SuperXAS beamline (SLS, Switzerland) under various reaction condition such as NO/NH_3 or NO/O_2 gas stream at temperatures ranging from 200-350°C d in fluorescence mode with a 5 s time resolution. The resulting large XAS dataset was analyzed with multivariate curve resolution analysis and subsequent *ab initio* modelling.

Results and discussion. *In-situ* XAS studies carried out in presence of NO/NH_3 or NO/O_2 at 350°C demonstrated the involvement of all iron atoms in the redox cycle and with that suggest that Fe species in the studied Fe/ZSM-5 catalyst are monomers, which was furthermore confirmed by EXAFS and UV-VIS spectroscopy. Ab initio simulation of the experimental X-ray absorption data, carried out using FDMNES, revealed that the single site Fe species in the sample obtained by this approach adopt a square planar geometry, which changes into five-fold coordination at low temperature by strongly binding to either NO or NH_3. This catalyst showed high activity in low temperature SCR compared to conventionally prepared Fe/ZSM-5. The presence of monomeric Fe species in this Fe/ZSM-5 convey molecular level insights into the temperature dependent NH_3-SCR activity and might prove useful in the study of other reactions over monomeric Fe species, such as methane partial oxidation or dehydroaromatization reactions.

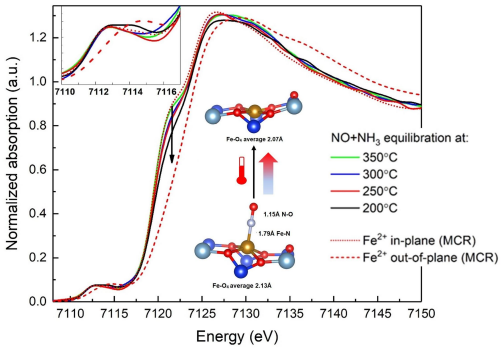

Figure 1 ***In-situ*** **XANES spectra recorded for Fe/dZ-EDTA catalyst at different T under a stream of NO/NH_3**

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Making Iron Active: Highly-loaded Bimetallic Iron-Cobalt Catalysts for Hydrogen Release from Ammonia

S. Chen[1], J. Jelic[2], D. Rein[3,4], S. Najafishirtari[1], F.-P. Schmidt[5], F. Girgsdies[5], L. Kang[3], A. Wandzilak[3], A. Rabe[1,4], D. E. Doronkin[2,6], K. Friedel Ortega[1], S. DeBeer[3], J.-D. Grunwaldt[2,6], R. Schlögl[3,5], T. Lunkenbein[5], F. Studt[2,6], and M. Behrens[1,4]*

[1]*Institute of Inorganic Chemistry, Christian-Albrechts-University Kiel, Germany*

[2]*Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Germany*

[3]*Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany*

[4]*Faculty of Chemistry, University of Duisburg-Essen, Essen, Germany*

[5]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Inorganic Chemistry, Berlin, Germany*

[6]*Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Germany*

mbehrens@ac.uni-kiel.de

Introduction. Ammonia, according to its high hydrogen content and energy density, convenient infrastructure for transportation and storage, is becoming a promising energy carrier. Hydrogen could be stored by synthesizing ammonia, afterwards released by ammonia decomposition. However, there is still a challenge in the design of a highly efficient catalyst for ammonia decomposition at mild conditions.[1] Recent studies revealed nitrogen desorption as being the rate-determining step on many transition metal catalysts, and explain the superiority of Ru catalyst by its moderate nitrogen binding energy.[2] Herein we present a synthesis route for Fe-based catalysts inspired by the highly-loaded Haber-Bosch catalyst, identify nitridation as the reason for its moderate activity and demonstrate how nitridation can be suppressed and a nitrogen binding energy similar to Ru can be reached by alloying with Co.

Experimental. All FeCo/MgO catalysts were prepared by co-precipitation of LDHs / hydroxides in an automated reactor system at various Fe:Co ratios. The precursors were calcined and further isothermally reduced in H_2. Activity tests were carried out in a flow reactor in a diluted gas (3% NH_3/He). Structural analyses of $Fe_{1-x}Co_x$/MgO catalysts were performed during the reduction process by *in situ* XRD and afterwards by *ex situ* STEM-EDX. *Operando* XAS measurements both at the Fe and Co K-edge were carried out at the CAT-ACT beamline at the KIT light source in Karlsruhe, Germany.

Results and discussion. High-loaded $Fe_{1-x}Co_x$/MgO samples were obtained from the reduction of spinel $Mg(Fe_{1x}Co_x)_2O_4$. XRD and STEM-EDX-mapping confirmed the formation of metallic Fe or FeCo alloy (loading ~60%) while the unreduced support material was identified as magnesium wuestite-like oxide. *In situ* XRD and XAS were performed to understand the reduction process. Considering the dispersions of mono-/bi-metallic NPs, $Fe_{0.75}Co_{0.25}$/MgO showed a similar TOF as $Fe_{0.5}Co_{0.5}$/MgO (~0.26 s^{-1}), which is higher than Fe/MgO (0.15 s^{-1}) and Co/MgO (0.13 s^{-1}) (Figure 1a). Hence, the bimetallic catalysts were more active than Fe or Co only, but higher Co content did not lead to a further improvement. *Operando* XAS measurements were performed on Fe/MgO and $Fe_{0.5}Co_{0.5}$/MgO catalysts. During the reaction, Fe/MgO showed 69% Fe_3N and 31% Magnesium wuestite without α-Fe while $Fe_{0.5}Co_{0.5}$/MgO showed 82% FeCo alloy and 18% Magnesium wuestite. Fe_3N on Fe/MgO was also identified in XRD after reaction, which was not observed on $Fe_{0.5}Co_{0.5}$/MgO. This indicates that iron is readily nitridated and the resulting nitrides have a negative effect, while the Fe-Co alloy was stable against nitridation. DFT calculations supported the nitridation of Fe and revealed that Fe_3N surfaces exhibit too weak binding energies and are thus less active. By alloying Fe with Co, this nitridation could be suppressed and the nitrogen binding energy is additionally influenced to shift to a moderate value, leading to a highly active and stable catalytic performance (Figure 1b).

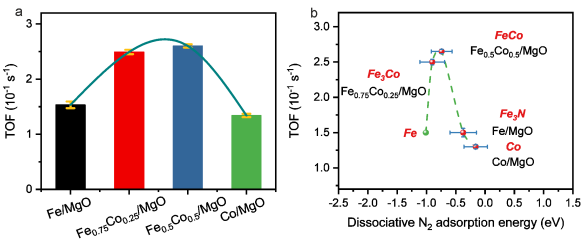

Figure 1. TOF of the four Fe_xCo_{1-x}/MgO catalysts for ammonia decomposition at 500C (a) and TOFs of the four Fe_xCo_{1-x}/MgO catalysts as a function of the corresponding dissociative N_2 adsorption energy (b), green dashed volcano curve considering the N_2 adsorption energy of pure Fe site and of Fe_3N.

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Surface Composition and Adsorption Dynamics in Fe-Co Ammonia Decomposition Catalysts

L. Kang[1], S. DeBeer[1*],

[1]*Department of Inorganic Spectroscopy, Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34-36, 45470 Mülheim an der Ruhr, Germany*

[*] *E-mail address: serena.debeer@cec.mpg.de*

Introduction.

The decomposition of ammonia has been brought into the focus of forefront research in recent years because ammonia has shown great potential as a potential energy storage molecule with high energy density and high hydrogen capacity. Currently, the ideal catalyst for ammonia decomposition is Ru-based due to the optimal N_2 adsorption energy, while the high cost of Ru limits its application at the industrial scale. One of the most promising candidates is Fe-based catalysts, but the activity and durability are still not comparable to the Ru-based catalysts. A speculative explanation is that Fe has much stronger chemical adsorption of N_2, which leads to the irreversible formation of iron nitride by dissociation of the triple bond of the produced N_2 on the surface. Therefore, the access of active Fe sites by NH_3 is inhibited in ammonia decomposition, leading to poorer catalytic performance. To prove this hypothesis, we studied two model catalysts, reduced $MgFe_2O_4$ and reduced $MgFeCoO_4$, and performed combined in situ AP-XPS and AP-NEXAFS characterizations to understand the electronic structure of catalysts surface upon redox/nitridation during catalysis.

Experimental/methodology.

In situ AP-XPS and AP-NEXAFS experiments were accomplished at the B07C beamline of Diamond Light Source. Catalysts sample powder was drop-casted on Au-coated Si wafers and mounted on a 'teapot' sample holder which has a built-in heater and thermocouple. The temperature of the sample was regulated between 298 and 873 K and the gas pressure was controlled between UHV and 1 mbar. The exhaust gas was analyzed continuously by a mass spectrometer. Fe/Co 2p XPS and N/O 1s XPS spectra were collected using excitation energy of 1025 eV and 1300 eV respectively to avoid interference from the Auger peaks. The Fe $L_{3,2}$-edge and Co $L_{3,2}$-edge NEXAFS spectra were measured in both total electron yield (TEY) mode using analyzer cone current and Auger electron yield (AEY). The Fe $L_2M_{23}M_{23}$ Auger emission at 592 eV and Co $L_3M_{23}M_{23}$ Auger emission at 648 eV were integrated for Fe $L_{3,2}$-edge and Co $L_{3,2}$-edge NEXAFS AEY-NEXAFS, respectively. Typical in situ conditions for XPS & NEXAFS include 1mbar H2 at 873K, 1mbar NH3 at 673K, 773K and 873K.

Results and discussion.

The reduction of surface Fe species, adsorption of NH_3 and N_2, as well as the formation of nitride, are observed in Fe 2p XPS, Fe L_3-edge NEXAFS and N 1s XPS respectively (Figure 1). Parallel studies on the more active and durable $MgFeCoO_4$ catalyst were also performed. With half of Fe but additional Co (which has weaker adsorption of N_2), the $MgFeCoO_4$ catalyst showed a much less significant reduction of Fe and the formation of nitride. Such a good correlation between the surface electronic structure and the catalytic activity provides solid evidence to support our hypothesis above and is inspirational to further mechanism studies for ammonia decomposition.

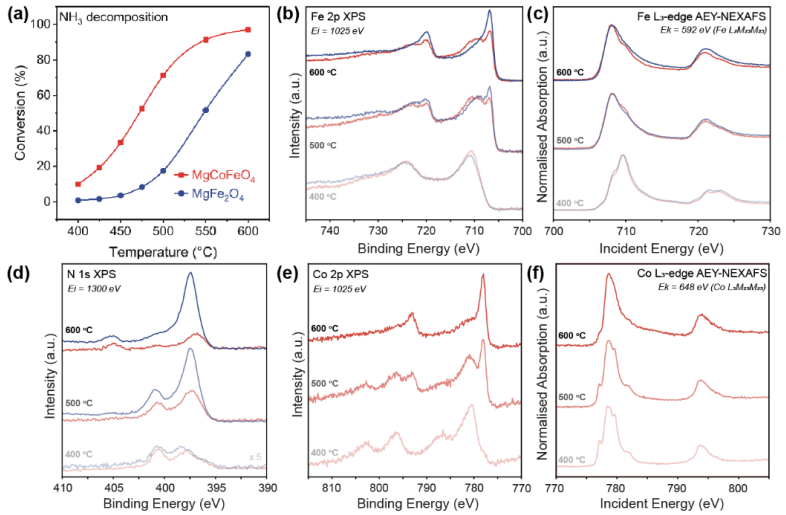

Figure 1. (a) Catalysis performance of Mg-Co-Fe catalyst (red curve) and Mg-Fe catalyst (blue) for NH_3 decomposition. *In situ* (b) Fe 2p XPS, (c) Fe L_3-edge AEY-NEXAFS and (d) N 1s XPS spectra of both catalysts during NH_3 decomposition at 673K, 773K and 873K respectively. In situ (e) Co 2p XPS and (f) Co L_3-edge AEY-NEXAFS spectra of Mg-Fe-Co catalyst during NH_3 decomposition at 673K, 773K and 873K respectively.

Acknowledgments

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Statistical Insights into Atomic Distributions in Single-Atom Catalysts through Machine Learning Assisted Image Analysis

S. Mitchell[1*], K. Rossi[1], D. Faust Akl[1], A. Ruiz Ferrando[2], F. Parés[3], V. Gimenez[3], X. Hai[4], J. Lu[4], D. GarciaGasulla[3], N. López[2], J. PérezRamírez[1]

[1]*ETH Zürich, Zürich, Switzerland*
[2]*Institute of Chemical Research of Catalonia, Tarragona, Spain*
[3]*Barcelona supercomputing center, Barcelona, Spain*
[4]*National University of Singapore, Singapore*
[*]*msharon@chem.ethz.ch*

Keywords: single-atom catalysis, atomic distributions, transmission electron microscopy, machine learning.

Introduction. Single-atom catalysts (SACs) have unique properties that can affect their reactivity and efficiency.[1] Aberration-corrected scanning transmission electron microscopy (AC-STEM) is the main technique used to study the spatial arrangement of atoms in SACs, which is crucial to confirm the atomic dispersion and can provide insight into the density and proximity of atoms. However, the process of analyzing these images is time-consuming and the results are often not statistically robust.

Methodology. Our study aims to improve understanding of atomic distributions in SACs by using machine-learning techniques to analyze AC-STEM images of materials with specific properties, and complementing the analysis with insights gained from atomistic models.

Results and discussion. We developed a convolutional neural network (SAC-CNN) that can rapidly and accurately detect atoms in AC-STEM images of SACs based on non-crystalline supports (**Fig. 1a**).[2] This presentation explores the general applicability of the model and highlights the advanced insights it can provide for the design of SACs (**Fig. 1b**), considering the relationship between the observed atomic distributions and the underlying features of the support and metal species.

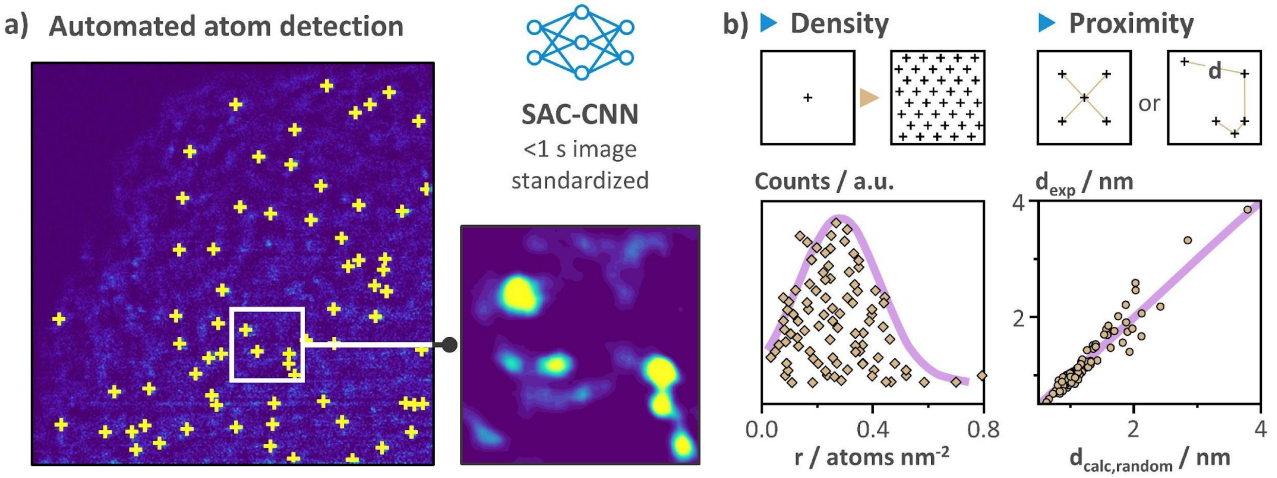

Figure 1. (a) AC-STEM image of a Pt_1/NC SAC indicating the metal atoms detected by the SAC-CNN model (yellow crosses). The model generates a probability map, shown for the white boxed area, to standardize the analysis of single-atom dispersions. (b) The possibility to rapidly assess large image sets can provide statistically relevant insights into previously inaccessible properties of SACs.

Acknowledgments
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Limits of Detection for EXAFS Characterization of Single Atom Catalysts

Jordan Finzel[1], Phillip Christopher[1]*, Simon R. Bare[2]*

[1]*Department of Chemical Engineering, University of California Santa Barbara*
[2]*Stanford Synchrotron Radiation Light Source, SLAC National Accelerator Laboratory*
*srbare@slac.stanford.edu; *pchristopher@ucsb.edu

Introduction. Single atom catalysts (SACs) attract attention due to their unique reactivity and precise chemical tunability. Authors often use – and reviewers often require – extended X-ray absorption fine structure (EXAFS) data to prove the absence of clustered metal (or metal-oxide, MO) structures under *in-situ* or *operando* conditions. However, there has been no critical assessment of the ability of EXAFS to substantiate such conclusive statements. Here we assess the ability of EXAFS to identify metal (oxide) clusters in catalysts containing predominantly SAs by modelling data for mixtures of atomically dispersed metals and metal or MO clusters. We quantify the fraction of metal species that can coexist with SA sites as either metal or MO clusters while eluding detection with any statistical significance. Additionally, through a descriptor-based screening approach we identify certain oxide structures for which differentiating atomically dispersed metal species and MO clusters would be infeasible by EXAFS.
Experimental/methodology. EXAFS were modelled using FEFF6 for a Pt/CeO_2 single atom site, a 0.6nm Pt_{13} metallic cluster, and a 1nm $Pt_{14}O_{37}$ oxidized. Datasets consisting of linear combinations of spectra from various species were fit using a robust model for the Pt/CeO_2 SAC structure described by 5 dominant scattering paths. The $\chi(k)$ was calculated for various bulk oxides using experimental crystal structures. Spectra were analyzed using a continuous Cauchy wavelet transform (CCWT), and the maximum of the modulus of the CCWT beyond 2Å was identified as a descriptor for detection of oxide clusters.
Results and discussion. To identify the limits of detection of clustered species that coexist with SAs using EXAFS, it is important to distinguish the scattering features of different types of sites. SAs on oxide supports typically contain metal-oxygen (M-O) and metal-oxygen-support (M-O-S) interactions, metallic clusters predominantly display metal-metal (M-M) interactions, and metal oxide clusters exhibit both M-O and M-O-M scattering (Figure 1a). As an example, we modelled EXAFS of Pt/CeO_2 SACs. Linear combinations (LCs) of Pt/CeO_2 SAC with metallic Pt_{13} clusters show clear changes as expected; (Figure 1b).

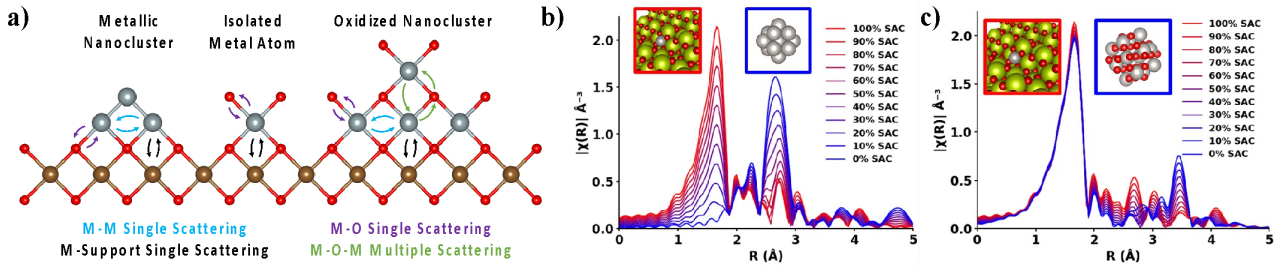

Figure 1. (a) Scattering paths for isolated metal sites (middle), and metallic (left) or oxidized (right) nanoclusters. Modelled FT EXAFS data for mixtures of Pt/CeO_2 SAC and (b) metallic Pt_{13} or (c) oxidized $Pt_{14}O_{37}$ clusters.

Conversely, LCs from the SAC structure and a 1nm $Pt_{14}O_{37}$ cluster do not show pronounced differences. Similar Pt-O bonding necessitates analysis beyond the first shell, which shows Pt-Ce scattering paths at ~2.75 Å when the SAC is the majority species (red), while scattering associated with Pt-O-Pt interactions on the oxidized Pt cluster (blue) become more apparent at ~3.4 Å (Figure 1c). Fitting these datasets with a model of the SAC site, the quality of the fit (the R-factor) quickly deteriorates when the metallic Pt_{13} cluster contributes as a minority species but is far less sensitive to the coexistence of the oxidized $Pt_{14}O_{37}$ cluster. Our results indicate that up to 40% of Pt may exist as oxidized clusters before being identified with any statistical significance. We also identified a descriptor based on a wavelet transform analysis – the CCWT modulus maximum – that trends well with the observed experimental prevalence of higher order scattering [1] and is necessary to differentiate SAC sites from metal oxide particles.

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Using Light to Sense the Local Temperature during Catalytic Reactions

T.S. Jacobs[1,*], F.T. Rabouw[1], B.M. Weckhuysen[1], W. van der Stam[1]

[1]*Inorganic Chemistry and Catalysis group, Debye Institute for Nanomaterials Science & Institute for Sustainable and Circular Chemistry, Utrecht University, Utrecht, the Netherlands*

[*]*t.s.jacobs@uu.nl*

Introduction. Catalysis operates on a broad range of pressures and temperatures, from ambient conditions to temperatures above 1000 K, depending on the catalyst and reaction of interest. Small variations in the overall reactor temperature are known to affect the catalytic performance. While local variations in temperature likely play an equally important role, these are rarely studied in detail.[1] To study local heat effects in catalytic reactions, temperature measurements over a broad temperature range and with a high spatial resolution are necessary.

Experimental/methodology. In this work, we use "luminescence thermometry" to study local temperatures during catalytic reactions.[2] Microcrystalline 1-μm-diameter Y_2O_3 particles doped with Nd^{3+} are mixed into the reactor bed. Nd^{3+} emits near-IR light with a temperature-dependent spectrum. We can thus determine local temperature variations by mapping the Nd^{3+} emission spectrum. By tuning the Nd^{3+} doping concentration for optimal signal strength, we achieve precise temperature readouts (error of <1 K) at temperatures relevant for various catalytic processes, including CO_2 hydrogenation performed at 673 K.

Results and discussion. We characterized spatial temperature heterogeneities with μm resolution during two catalytic processes. The exothermic CO_2 methanation reaction (Figure 1a, using a Ni/TiO_2 catalyst, ΔH_r = –165 kJ/mol) was studied at 673 K. Pulsing the reactant gasses (*e.g.,* CO_2) causes a temperature jump of +9 K on average, with a wide variations over a region as small as 35×35 μm^2 (Figure 1b). The formation of products (*e.g.*, CH_4) in the thermocatalytic reactions was detected with on-line mass spectrometry (MS) and correlated to the observed heat profile. Next to the thermocatalytic conversion of CO_2, these thermometers were also applied to CO_2 electroreduction at room temperature. An applied current density of –50 mA/cm^2 resulted in a temperature increase of +10 K. These applications of the luminescence thermometry sensor shine light on the temperature heterogeneity during catalysis.

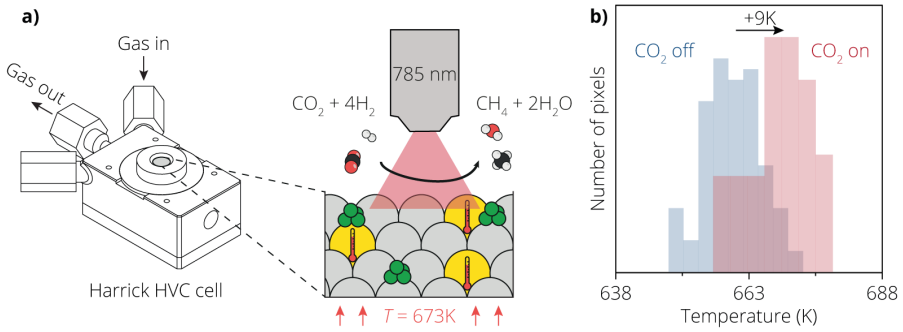

Figure 1. a) Reactor setup with the Ni/TiO_2 catalyst (green and grey, respectively), mixed with the thermometers (yellow). b) Measured temperature distributions over an area of 35×35 μm^2 with pixel size of 3.5×3.5 μm^2, before and during the introduction of reactant gasses, showing the exothermicity of the CO_2 methanation reaction with an average temperature increase of +9 K.

Acknowledgments

This research was carried out under project number C19017 in the framework of the Research Program of the Materials innovation institute (M2i) (www.m2i.nl) and received funding from the Dutch Research Council (NWO) in the framework of the ENW PPP Fund for the Topsectors and from the Ministry of Economic Affairs in the framework of the "PPS-Toeslagregeling".

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Hard-Soft MCR-ALS of IR spectroscopic isotherms: an innovative method for the characterization of adsorption at the molecular scale.

R. Aboulayt,[1] P. Bazin,[1] A. Vimont, [1] S. Maury,[2] C. Chizallet,[2] A. Travert*

[1] *Normandie Univ, ENSICAEN, UNICAEN, CNRS, LCS, 14000 Caen (France)*

[2] *IFP Energies nouvelles, Direction Catalyse, Biocatalyse et Séparation, BP3, 69360 Solaize (France)*

**arnaud.travert@unicaen.fr*

Introduction. Classical quantitative analytical methods for the characterization of adsorbents such as gravimetric analysis or calorimetry yield values averaged over the various adsorption sites[1]. Here, In situ IR spectroscopy combined with multivariate analysis has been used to identify and characterize quantitatively alcohol adsorption on zeolites.

Experimental/methodology. Spectroscopic isotherms (IR spectra vs pressure, fig.1a) at various temperatures were recorded and analyzed by using multivariate curve resolution analysis (MCR-ALS)[2] implemented in SpectroChemPy[3].

Results and discussion. Hybrid hard soft MCR-ALS, used for the first time in the field of adsoption, allowed us to recover pure response profiles: spectral profiles (fig.1b), allowing identification of distinct species on the basis of their spectra, and adsorption isotherms (fig.1c), allowing to assess sorption parameters by curve fitting a local isotherm such as the Langmuir isotherm or implementation of the isotherm as a hard constaint.

As shown in Figure 1, in the case of the adsorption of isobutanol on MFI zeolites, three species could be identified, in particular by analysis of the ν(OH) range: adsorption on bridged OH groups (#1), on extra-framework Al-OH (#2) and on silanol groups (#3). Analysis of the adsorption isotherms at various temperatures allowed recovering the corresponding adsorption enthalpies; $\Delta_{ads}H$ $\Delta_{ads}H$ (#1) ~ -110 kJ/mol; $\Delta_{ads}H$ $\Delta_{ads}H$ (#2) ~ -90 kJ/mol; $\Delta_{ads}H$ $\Delta_{ads}H$ (#3) ~ -30 kJ/mol.

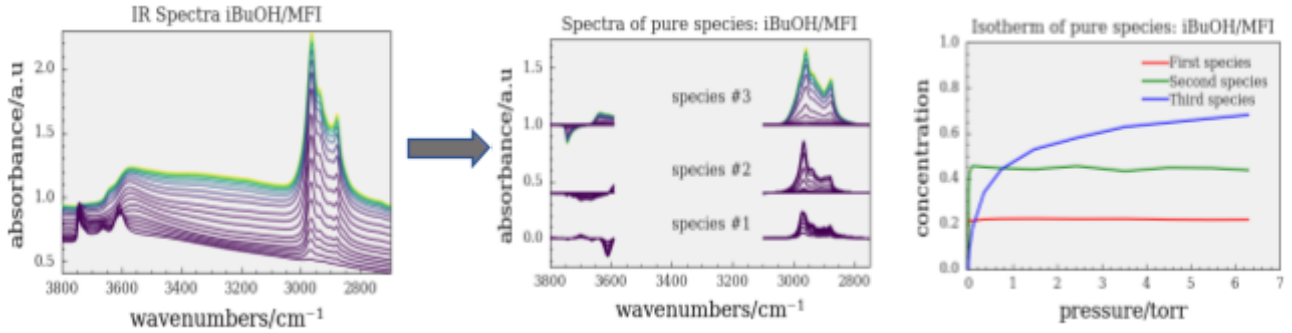

Figure SEQ Figure * ARABIC 1: MCR-ALS output -Spectra and concentration of pure species (iBuOH/MFI)

In conclusion, the present methodology has the potential to provide unique insights into the assessment of adsorption properties of complex zeolite-based catalysts. Its limits, advantages and drawbacks with respect to conventional methods will be discussed.

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Hard X-ray Nanotomography Reveals Coking in Technical Catalysts

S. Weber[1,2], A. Diaz[3], D. Karpov[3], M. Kahnt[4], Y. Romanenko[2], S. Kotrel[5], J.-D. Grunwaldt[1], S. A. Schunk[2,5], T. L. Sheppard[1*]

[1]*Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*
[2]*hte GmbH, Heidelberg, Germany*
[3]*Paul Scherrer Institut, Villigen PSI, Switzerland*
[4]*MAX IV Laboratory, Lund, Sweden*
[5]*BASF SE, Ludwigshafen, Germany*
[*]*thomas.sheppard@kit.edu*

Keywords: characterization, X-ray tomography, deactivation, coking, dehydrogenation

Introduction. Understanding the deactivation of industrial catalysts is highly important for rational design of more stable catalysts. During light alkane dehydrogenation, coke formation is considered as major deactivation pathway requiring frequent regeneration cycles.[1] As industrially applied catalysts usually exhibit a complex 3D structure, e.g., involving binder materials to formulate macroscopically shaped catalysts, bulk analysis methods may only provide limited or unrepresentative information.[2] Recently, spatially-resolved hard X-ray tomography studies could identify coked regions of single catalyst grains, although the resolution was not high enough to probe accessibility of different regions in the catalyst particles.[3,4] Here we outline a study with complementary tomography methods to address this problem.

Experimental/methodology. An industrial propane dehydrogenation catalyst consisting of zeolite and amorphous silica binder was studied at different aging stages (Figure 1). Ptychographic X-ray computed tomography (PXCT) was performed for each catalyst at PSI – cSAXS beamline. Additionally, the fresh and harsh aged sample were impregnated with Cu solution serving as a fluorescent marker. These impregnated samples were studied by X-ray fluorescence tomography (XRF-CT) at MAX IV – NanoMax beamline.

Results and discussion. The combination of PXCT and XRF-CT enables to locate regions of coking and reveal pore accessibility in 3D space. PXCT provides quantitative information about electron density of the studied samples. This can be used to distinguish between binder and zeolite phases within the catalyst particles. Coke species formed in the pores lead to an increasing electron density. PXCT revealed that coke is predominantly formed within the pores of the binder and not the zeolite, but the resolution is not sufficient to probe the accessibility of pores. Complementary XRF-CT shows that the overall uptake of Cu ions used as fluorescent markers is reduced by more than 90 % comparing the harsh aged to the fresh sample. This reveals an important distinction that mainly coking of the binder phase leads to deactivation of the catalyst, not coking of the active zeolite component, even though the results of coking on the fate of the catalyst performance may be similar. The findings allow a future rational tailoring of the catalyst towards higher stability by increasing the coking resistance of the binder, highlighting the unique information available to hard X-ray tomography which cannot be obtained with contemporary characterization methods.

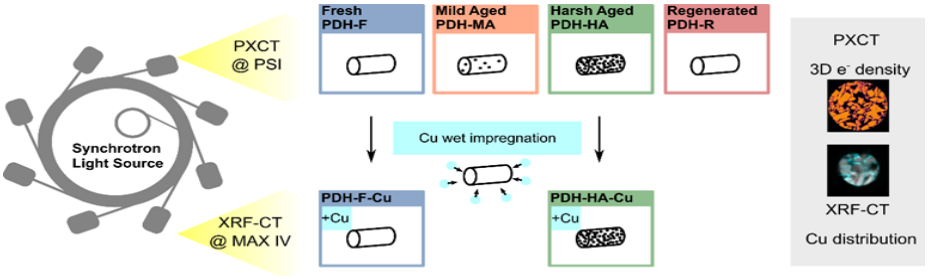

Figure 1 Overview on the studied samples and applied characterization methods with their related information.

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Tracking surface processes on water oxidizing anodes using high-sensitivity *operando* ellipsometry

K. Frey[1*], J. S. Pap[1], D. Lukács[1], Z. Lábadi[2], D. Mukherjee[2], N. Szász[3], M. Németh[1], P. Petrik[2]

[1] *Surface Chemistry and Catalysis Department, Centre for Energy Research, Hungary*

[2] *Photonics Department, Centre for Energy Research, Hungary*

[3] *Thin Film Physics Department, Centre for Energy Research, Hungary*

Corresponding Author's E-mail address: frey.krisztina@ek-cer.hu

Keywords: operando ellipsometry, water splitting, electrocatalysis

Introduction

The reduction-oxidation transformations in the nm-thick diffusion layer near the electrode surface can be characterized by the Faraday current, or, by *in situ* probing methods. We used for the first time *in situ* ellipsometry [1] to study the sub-nanometer thick film formation of an anode catalyst in a quantitative and time-resolved way.

Experimental/methodology

Novel catalytic systems for water splitting use 1st row transition metals – including molecular catalysts – instead of noble metals. Several of our oxygen-producing anode catalysts alter during use, demonstrated *via* electrochemical characteristics, low-resolution solution spectroscopy, or *ex situ* surface analysis. The rapid initial processes, *e.g.*, molecular precursor decomposition and formation of a stable, catalytically active film on the electrode, are difficult to study and therefore they remained less explored so far [2,3]. The present study explored the initial stage of film formation from a molecular Cu-peptide pre-catalyst [3], and the dependence of the film properties on the applied potential.

Results and discussion

In situ ellipsometry established a correlation between the identified redox transformations and the film formation. The electrochemical-ellipsometric cell accommodated our indium tin oxide (ITO) or fluorine-doped indium oxide (FTO)-coated working electrodes used for the catalysis and an electrolyte with a composition optimized in our earlier study [3]. Electrochemical processes were controlled with a potentiostat-galvanostat. The solution layer at the working electrode was probed by ellipsometry, giving the thickness, depth-inhomogeneity with 0.5 nm resolution, and quantitative spectral properties of the resulting film; this has been corroborated by SEM and XPS measurements.

Acknowledgements

We are thankful for the funding of the National Research, Innovation and Development Office of Hungary, grant numbers NKFI-128841, TKP2021-NKTA-05 (J.S. Pap) and TKP2021-EGA-04 (P. Petrik). Support from OTKA K131515 and ELKH EK grants are highly acknowledged.

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In-Situ Operando and Ex-Situ Study on Light Hydrocarbon-Like-Diesel and Catalyst Deactivation Kinetic and Mechanism study During Deoxygenation of Sludge Oil

G. Abdulkareem-Alsultan[1,2*], N. Asikin-Mijan[3], Robiah Yunus[2], Yun Hin Taufiq-Yap[1,4]

[1]*Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Kota Kinabalu 88400, Sabah, Malaysia*

[2]*Department of Chemical and Environmental Engineering, Universiti Putra Malaysia (UPM), 43400 Serdang, Selangor, Malaysia;*

[3]*Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor Darul Ehsan, Malaysia*

[4]*Catalysis Science and Technology Research Centre (PutraCat), Faculty of Science, Universiti Putra Malaysia, UPM, Serdang 43400, Selangor, Malaysia*

Keywords: Manganese; cobalt; catalyst deactivation; steady-state rate; deoxygenation

Introduction: Deoxygenation is a highly significant means of generating oxygen-free hydrocarbon fuels from liquid biomass. This study will deoxygenate sludge palm oil (FFA % = 42.35%) in an H_2-free atmosphere through a series of Mn-Co supported AC catalysts ($MnO_{0.5}CoO_{0.5}$/AC, $Mn_{0.5}Co_{0.5}S$/AC and $Mn_{0.5}Co_{0.5}P$/AC). The XAS in-situ results confirm that the preparation method of formation the catalyst structure was successful.

Results and disscusion: The catalytic results show that by oligomerizing unsaturated fatty acids produced during Diels-Alder reactions or radical additions, the $MnO_{0.5)}CoO_{0.5}$/AC can largely enhance the production of heavy products. It is a straightforward process to transform these heavy products into coke species, which enables the rapid deactivation of the catalyst. This study additionally showed that AC-supported sulphide and phosphide Mn-Co catalysts are hugely beneficial for steadily and reliably acquiring an above-average yield of diesel-range hydrocarbons at substantially reduced temperatures whilst simultaneously effectively impeding catalyst deactivation during deoxygenation. The deactivation kinetic study conform that the deactivation happens by the coke formation and flow the second order deactivation In this work, the effects that different catalyst structures have on deactivation and yield have been thoroughly investigated by deoxygenating several catalysts, including $Mn_{0.5}Co_{0.5}P$/AC, $Mn_{0.5}Co_{0.5}S$/AC, and $MnO_{0.5}$ $CoO_{0.5}$ /AC. In this study, the reactant feedstock was sludge palm oil with a high acid value and FFA content in excess of 95%. The feedstock oil was comprised of fatty acid units (both saturated and unsaturated). The results indicate that each of the three catalyst types successfully deoxygenated the feedstock by removing the oxygen in the forms of carbon monoxides, carbon dioxides, and water. What's more, the results show that the formation of heavy products during the oligomerisation of unsaturated fatty units when Diels-Alder reactions or radical additions are carried out is substantial. However, the application of metal oxide and metal sulphide catalysts can improve this by converting hydrogen into coke species. This is a relatively simple process. In this context, this study demonstrated that metal phosphide supported catalyst for deoxygenation has two significant advantages. First of all, it plays an important role in producing higher yields of diesel range n-hydrocarbon. Secondly, it can be effective in slowing down catalyst deactivation caused by the build-up of coke.

Copper-nickel deoxygenation catalysts
Part I: Reducicbility and surface area

K. Pacultová[1], K. Karásková[1], D. Fridrichová[1], T. Bílková[1], J. Aubrecht[2], B. Shumeiko[2], D. Kubička[2]

[1]*Institute of Environmental Technology, CEET, VSB-Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava, Czech Republic*

[2]*Department of Petroleum Technology and Alternative Fuels, University of Chemistry and Technology Prague, Technická 5, Prague 166 28, Czech Republic*

Keywords: copper-nickel catalysts, specific surface area, metal surface area, reducibility

Introduction. Copper-nickel catalysts represents a catalytic system suitable for converting of biomass-derived feedstocks into sustainable chemicals or biofuels. The advantage of the transitional metals is, besides their affordable price, the ease of the preparation, possibility to prepare different bimetallic compositions having diverse interactions with the support and, thus, different reducibility and metal dispersion resulting in tunability of their catalytic properties.

Experimental/methodology. Ni/Al_2O_3, Cu/Al_2O_3 and bimetallic $Ni\text{-}Cu/Al_2O_3$ catalysts varying in Cu and Ni content were prepared using wet impregnation. Metal oxides reducibility was studied by temperature programmed reduction by hydrogen ($TPR\text{-}H_2$). The number of surface nickel sites was determined by hydrogen pulse chemisorption and copper surface area was obtained by reactive frontal chromatography (N_2O chemisorption). Specific surface area was evaluated by N_2 physisortion.

Results and discussion. Both metal sites, nickel as well as copper are accessible at the catalyst surface after a reductive treatment. The number of accesible surface sites depends on the reduction temperature and the respective metal content in the sample. However, the reducibility is strongly influenced by metal support interactions as well as by interactions between the individual metals in the bimetalic catalysts (Fig. 1).

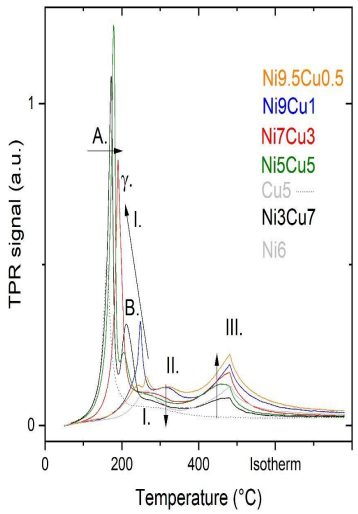

Fig. 1: $TPR\text{-}H_2$ of $Cu\text{-}Ni/Al_2O_3$ catalysts (ambient to 480 °C + 1 h isotherm). Peak A, B: Cu species, Peak γ: Cu+Ni species, Peak I - III: Ni species.

Acknowledgments

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Dynamics of metal-support electron transfer: an XFEL study

H.Gu[1], Y.Ren[1], Z.Wang[1], S.H. Park[2], S.Kwon[2], F.R.Wang[1*]

[1]*Department of Chemical Engineering, University College London, London, UK*

[2]Soft X-ray, PAL-XFEL

ryan.wang@ucl.ac.uk

Keywords: electron transfer, metal support interaction, XFEL, pump-probe XAS

Introduction. A turnover in catalysis happens between the ms to s scale. However, an elementary step within a turnover can be as short as ps to fs second scale. It is therefore important to shoot a complete molecular movie of a catalytic process. Such understanding will improve the catalyst design towards better activity and selectivity. Here we report the dynamics of metal (Cu) – support (CeO_2) electron transfer during a catalytic process with an X-ray free electron laser (XFEL). The electron transfer from Ce^{3+} to Cu^{2+} takes **2 ps**[1-2] This result indicates the electron donation from CeO_2 support is almost instantaneous and explains the role of widely used Ce^{3+}/Ce^{4+} redox pair in catalysis, such as the three-way catalyst and solid oxide fuel cell.

Experimental/methodology. 2wt% CuO-CeO_2 catalysts are prepared *via* a hydrothermal method.[3] The catalysts are pumped with a 267 nm laser (150 fs width) and probed with an X-ray pulse (150 fs width) with energy between Ce M_5 and Cu L_3 edges (850 to 940 eV). The delay time is set between the X-ray pulse and the laser pulse. Auger electrons emitted from the sample are collected (AEY mode) to measure the ground and excited states of Ce M_5 and Cu L_3 edge X-ray absorption spectroscopy (XAS).

Results and discussion. Upon excitation of 267 nm laser, two reactions proceed:

$$h\nu + Ce^{4+} + O^{2-} \longrightarrow Ce^{3+} + O^{-} \qquad \text{eq.1}$$

$$Ce^{3+} + Cu^{2+} \longrightarrow Ce^{4+} + Cu^{+} \qquad \text{eq.2}$$

The first reaction is a photochemical reaction whereas the second reaction is a typical support-metal redox reaction. To determine the dynamics of both reactions, First, the difference in Ce M_5 edge XAS between the ground and excited state is studied at Ce M5 edge (Fig. 1a). At 0.2 ps delay time, a decrease of Ce^{4+} intensity and an increase of Ce^{3+} intensity is observed, confirming the presence of eq. 1. Second, the difference in XAS intensity between excited and ground states at Ce^{3+} and Ce^{4+} features are studied by varying the pump-probe delay time (Fig. 1b,c). The Ce^{3+} excited state arrives within 200 fs, indicating the dynamics eq.1 is below 200 fs. The excited Ce^{3+} decays via electron transfer to Cu^{2+} (eq.2) with an overall process within 2 ps (Fig. 2b). Third, the Cu^{2+} dynamics is studied at Cu L_3 edge, also showing the reduction of Cu^{2+} within 2 ps. Combining both the dynamics of Ce^{3+} and Cu^{2+}, we confirm that eq.2 requires 2 ps only.

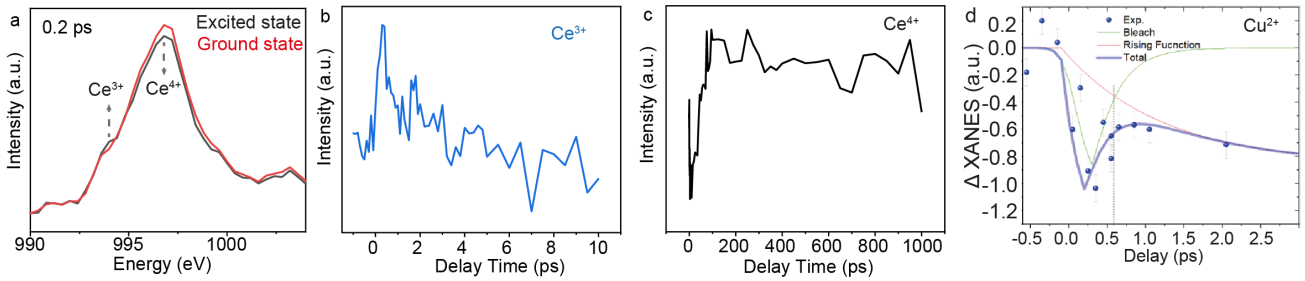

Figure 1. a Ground and excited state Ce M_5 edge XAS at 0.2 delay time. **b-d,** The difference between excited and ground state intensity of **b**, Ce^{3+}, **c**, Ce^{4+} and **d**, Cu^{2+} in the Ce M_5 and Cu L_3 XAS as a function of pump-probe delay time.

Our study is the very first step to shooting the molecular movie of a complete catalytic process. With more XFEL facilities and beamtimes available, the understanding of catalysis fundamentals will be significantly improved.

Acknowledgments. *We acknowledge PAL-XFEL facility for the pump-probe experiments conducted under proposal 2021-1st-SSS-004, 2021-2nd-SSS-011 and 2022-2nd-SSS-005.*

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In situ XAS and XES studies of Cu-CHA catalysts for Selective Catalytic Reduction (SCR) Reaction

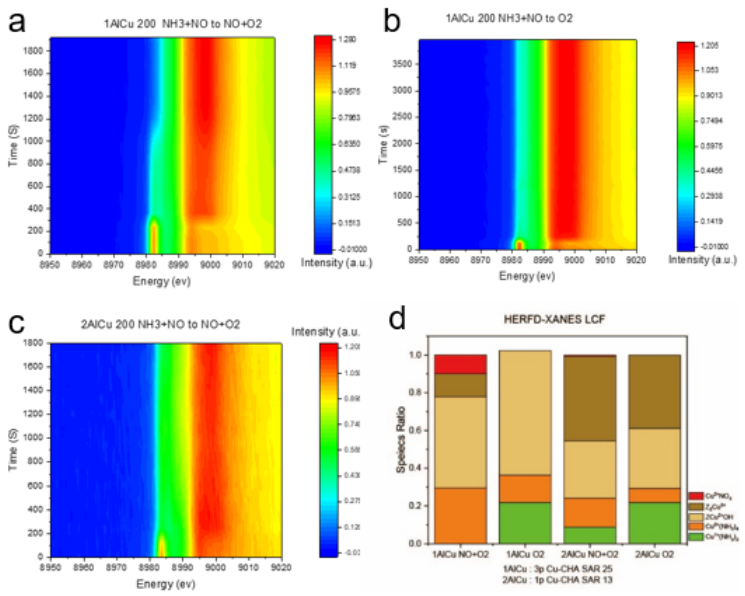
Zhipeng Wang, Prof. Ryan Wang

Keywords: Cu-CHA, SCR, Nitrate, X-ray Absorption Spectroscopy, X-ray Emission Spectroscopy

Introduction. NH3-selective catalytic reduction (SCR) of NO is an effective method to meet the EU07 standards in 2027. The commercial Cu-CHA system still face challenges at low temperature, in particular the oxidation half cycle (OHC). Two different Cu active species were analyzed by *in situ* X-ray Absorption spectroscopy (XAS), High energy resolution detection fluorescence- X-ray absorption near edge spectroscopy (HERFD-XANES) and valence to core-X-ray Emission Spectroscopy (VtC-XES). Based on our understanding in heterogeneous catalysis, the reaction mechanisms are structure dependent so different active sites will favour different reaction mechanisms. In the Cu-CHA catalyst, at high Cu loading, there are a variety of Cu active sites with different structures. Those active sites have different ways of breaking O-O bond, including the dimer and nitrate mechanisms.

Experimental/methodology. The oxidation half cycle can be studied by switching from reductive NO + NH_3 atmosphere to NO + O_2 or pure O_2. The comparison between these two conditions can determined the role of NO in the $Cu^{II}NO_x$ mechanism. 1AlCu (3%Cu-CHA SAR25) and 2AlCu (1%Cu-CHA SAR13) were studied with time resolved *in situ* XAFS.

Results and discussion.



Heat map (Figure a,b,c) and Linear Combination Fitting (LCF) result (Figure d) for 1AlCu and 2AlCu in different gas conditions

At low Cu loading (< 1wt%) and 200 °C, the Cu is mainly in the form of 2AlCu and the reaction proceeds with dimer mechanism. This is based on the linear relation between $(Cu/Al\ ratio)^2$ and SCR rate as reported in literature. At high Cu loadings (> 1wt%) and 200 °C, a variety of 1AlCu, 2AlCu and CuO clusters are formed, leading to different reaction pathways that contain single-site (nitrate), dimer and cluster mechanisms. At 400 °C, regardless of Cu loading, the linear relation between $(Cu/Al\ ratio)^2$ and SCR rate is no longer observed. The Cu site is no longer mobile and coordinates with the framework oxygen. Therefore, both nitrate and cluster mechanisms are possible and dimer mechanism is less likely to happen.

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Evolution of Chemical States of Pt during CO Oxidation over the Pt/CeO_2 Dominated with Pt-O-Ce and PtOx

Mingzhi Wang, Yige Zhang, Zhuangzhuang Wu, Yanping Zheng, Zhaohui Zhou, Weizheng Weng*

State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, PR China

Keywords: Ionic Pt, PtOx, metallic Pt, CO oxidation, *in situ* IR

Introduction. CeO_2 supported Pt catalysts play an important role in exhaust emission catalysis. Because of the interactions between catalyst and reactants under complex reaction conditions, Pt species may exhibit dynamic structural changes as a function of the reactant pressure and reaction temperature, making it difficult to determine the structure-performance relationship. In this study, the chemical states and dynamics of several typical Pt species, including PtOx, Pt–O–Ce and reduced Pt nanoparticles (NPs), in CO oxidation reaction and their correlations with activity were explored.

Experimental. The Pt/CeO_2 catalysts with Pt loading of 1wt% were prepared by impregnation method using H_2PtCl_6 (CPA), $(NH_4)_2PtCl_6$ (AHCP), $(NH_4)_2PtCl_4$ (ATCP), $(NH_3)_4Pt(NO_3)_2$ (TAPN) and $(NH_3)_4PtCl_2$ (TAPC) as precursors. After impregnating for 24 h, the samples were dried at 80 ºC and calcined in 21%O_2/N_2 mixture at 400 ºC for 4 h with a heating rate of 2 ºC/min. The obtained catalysts are denoted as Pt/CeO_2(CPA), Pt/CeO_2(AHCP), Pt/CeO_2(ATCP), Pt/CeO_2(TAPN), and Pt/CeO_2(TAPC). CO oxidation activity measurements were performed in a fixed-bed quartz tube reactor with 5 mm inner diameter using 1%CO/1%O_2/He (30 mL/min) as reaction feed. The reactor containing 50.0 mg catalyst was heated from 20 ºC to 350 ºC at a rate of 2 ºC/min with subsequent cooling and repeated heating in the reaction mixture.

Results and discussion. Based on the results of Raman, H_2-TPR and O_2-TPD characterizations, it can be concluded that the Pt/CeO_2 catalysts prepared with anionic Pt precursors (i.e. CPA, AHCP, ATCP) generate mainly Pt–O–Ce species that interact strongly with CeO_2, while those prepared with cationic Pt precursors (i.e. TAPN, TAPC), the PtOx species with relatively weak interaction with the CeO_2 are mainly formed. It was found that, for the CO oxidation over the oxidized catalysts, the Pt–O–Ce species with strong Pt–O bonds remained in the ionic state during the light off reaction, while PtOx species that interacted weakly with CeO_2 could be easily reduced to metallic Pt, which also exhibited better activity due to the enhanced reducibility of the Pt NPs-CeO_2 interface. Although the initial activity of the Pt/CeO_2 catalyst can be improved through reduction with H_2, the metallic Pt NPs, especially derived from the reduction of Pt–O–Ce dominated catalysts, can get reoxidized to the less active Pt^{n+}–O–Ce (n = 2–δ) species during the light off reaction (Fig. 1 & 2). A detailed *in situ* characterization revealed that the oxidation of metallic Pt NPs arises from oxygen reverse spillover from the CeO_2 support. This study shows that understanding the reaction-driven structural dynamics of Pt species is essential for exploring the reaction mechanism and elucidating how the catalyst is activated and deactivated in the reaction.

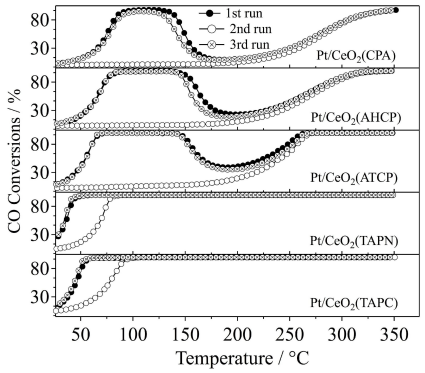

Fig. 1 CO conversions vs. temperature on the H_2 reduced catalysts.

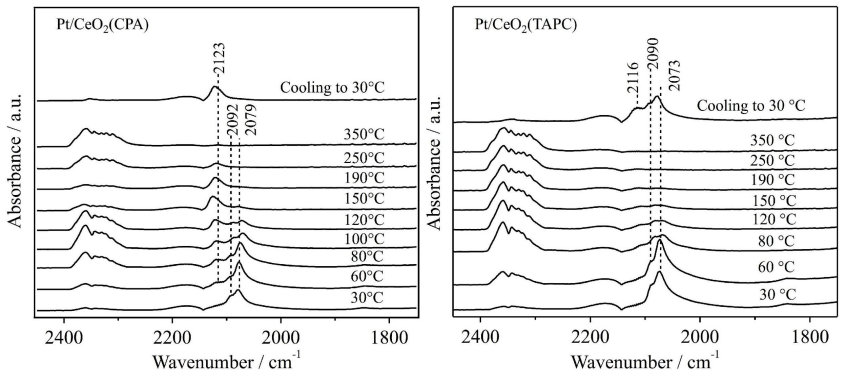

Fig. 2 CO oxidation reaction monitored by *in situ* FTIR spectroscopy on the H_2 reduced catalysts.

Acknowledgments

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Monitoring reduction process of supported Pd nanoparticles with hydrogen by operando ^{1}H NMR spectroscopy

Begum Yilmaz[1], Ersen Mete[2], Deniz Uner[1*]

[1] *Department of Chemical Engineering, Middle East Technical University, Cankaya 06800, Ankara, Turkey*
[2]*Department of Physics, Balikesir University, Balikesir 10145, Turkey*
[*]*uner@metu.edu.tr*

Keywords: PdH, ^{1}H NMR, DFT, Pd@PdO core shell

Introduction. ^{1}H chemical shift of the β phase over powdered palladium as a function of hydrogen pressure to be in between 20-34 ppm between vacuum and atmospheric pressure was reported by various studies[1]. Less commonly, a shielded peak is reported by solid state ^{1}H NMR studies in the literature[2] and assignment of this signal to α-PdH was discussed[3]. Herein, we report an experimental and DFT study which was conducted to reveal nature of the ^{1}H NMR chemical shifts of α and β PdH phases in Pd/TiO_2.

Experimental/methodology. A home-built high-vacuum glass manifold was used to probe H_2 adsorption under *in situ* conditions where the catalyst (10wt% Pd/TiO_2) resided in the sample chamber of a 43 MHz Magritek Spinsolve NMR spectrometer. NMR data was collected using Spinsolve Expert Software. For DFT calculations, we used projector augmented wave (PAW) method as implemented in VASP (Vienna *Ab-Initio* Simulation Package)[4]. The DFT–NMR chemical shift calculations were performed based on the linear response GIPAW method[5].

Results and discussion. In situ NMR measurements revealed that the appearance of the shielded peak at ~ -20ppm (Figure 1- left) was only observable if PdO was partially reduced. The results supported DFT estimations revealing similar NMR chemical shifts due to hydrogen adsorbed at the interface between the metallic core and surface segregated oxide layers of palladium (Figure 1 - right). For fully reduced Pd, DFT estimations shows a linear dependency of ^{1}H chemical shifts for 0.02≤H/Pd ≤1, due to the anionic character of hydrogen atom within the local electronic structure. This result posed an additional coverage dependency on the β hydride signal in addition to the fast exchange interpretations between β hydride and α hydride phases. This finding was also supported by the ^{1}H NMR spectra of β PdH collected at higher pressures (not shown).

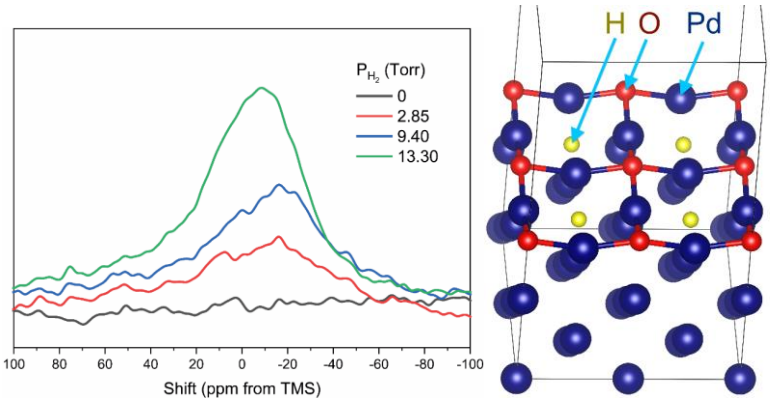

Figure 1. ^{1}H NMR spectra (left) over pre-reduced 10wt% Pd/TiO_2 under low H_2 pressures give rise to a shielded resonance, DFT estimations of the NMR shifts assign this resonance to protons accomodated between a metallic core and oxide shell (right)

Acknowledgments

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Identifying active centres of the VPO catalyst

F. Wolf,[1] C. Kaul,[2] A. Myachin,[2] K. Durner,[1] I. Kappel,[3] A. Beck,[2] S. Boecklein,[4*] S.-H. Park,[3] W.W. Schmahl,[3] G. Mestl,[4*] J. van Bokhoven,[2] J. Wintterlin.[1]

[1] *Department Chemie, Ludwig-Maximilians Universität München, Butenandtstr. 5 - 13, 81377 München.*
[2] *Institut fuŕ Chemie- und Bioingenieurwissenschaften, ETH Zuŕich, Zuŕich 8092, Switzerland.*
[3] *Department für Geo- und Umweltwissenschaften, Ludwig-Maximilians Universität München, Theresienstr. 41, 80333 München.*
[4] *Clariant Produkte (Deutschland) GmbH, Waldheimer Str. 13, 83052 Bruckmühl, Germany.*
[*] *sebastian.boecklein@clariant.com*
[*] *gerhard.mestl@clariant.com*

Introduction. With a world production of more than 2.75 million tons of maleic anhydride (MA) in 2018[1] and an expected growth rate of 6.7 % until 2025,[2] MA represents one of the key intermediates in chemical industry. Since the 1970's, the ternary vanadium phosphorous oxide (VPO) system is well known for its catalytic activity in the partial oxidation of *n*-butane to MA. However, despite this high economic importance, and approx. 50 years of research, a clear picture of the atomistic details of both the reaction mechanism and the respective active catalyst surface is still lacking. Part of the problem is the inherent complexity and chemical flexibility of the V-P-O system that makes a comparison of VPO catalysts of different origins extremely challenging.

Experimental/methodology. Industrially the VPO catalyst's activity is reversibly reduced in the process by continuously co-dosing a P containing species e.g. trimethyl phosphate (TMP) at a ppmv level. [3] Since such low amounts of P-species already result in a decisive reduction of activity, these P-species have to directly interact with the active centres on the VPO surface. This interaction is utlizied in the present study to gain knowledge about the active centres on a state-of-the-art inductrial VPO catalyst (SynDane®) via selective poisoning at different P levels. This way of modifying the catalyst surface led to a series of differently active VPO catalysts without any changes in the preparation that could impact the catalyst performance as well.
Using this approach, we report a multi-method approach with complementary techniques (XPS, FTIR, SEM, XRD, TG-MS) to identify and analyse active centres for the activation of *n*-butane on the VPO catalyst surface.

Results and discussion. Kinetic measurements done on fully equilibrated VPO catalysts after P poisoning confirms that such a P-treatment leads to a reduction of the active centres for the *n*-butane activation without changing the reaction barrier. At higher P-dosing, the appearance of a highly active but unselective surface state is detected. Via an analytical multi-method approach, this state of the catalyst is related to the appearance of β-$VO(PO_3)_2$. FTIR measurements with CO as probe molecule on all the differently P-doped VPO catalysts reveal several surface adsorption sites. A thorough deconvolution of the IR dataset and quantitative comparison with the P surface concentration and the kinetic data identifies two CO adsorption species being directly correlated with the active sites for *n*-butane activation! A deeper analysis of the FTIR spectra allows first speculations about the number and chemical nature of these sites responsible for *n*-butane activation on the VPO surface.

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Ball-milled CeO_2-CuO catalysts for methane activation: an *in-situ* DRIFT / *operando* NEXAFS study

R.Calligaro[1*], S.Mauri[2], C. F. Pauletti[3], M. Farnesi Camellone[2], S. Piccinin[2], M. Boaro[1], L. Braglia[2], P. Torelli[2], A. Trovarelli[1]

[1]*Dipartimento Politecnico, University of Udine, Udine, Italy*
[2]*CNR- Istituto Officina dei Materiali, Trieste, Italy*
[3]*Dipartimento di Fisica, University of Trieste, Trieste, Italy*

[*]*calligaro.rudy@spes.uniud.it*

Keywords: Ball milling, Ceria, Ce^{4+}/Cu^{+} interfaces, methane activation, *in-situ* DRIFT, *operando* NEXAFS,.

Introduction. Ceria/Copper interfaces are of particular interest because of their unique capacity to activate small molecules for their valorization.[1,2] In this work ceria-copper composites were prepared by ball milling on the hypothesis that mechanical energy may facilitate a charge transfer between Ce^{3+}/Ce^{4+} and Cu^{2+}/Cu^{+} redox couples. This contributed to create catalytic sites with superior reactivity in methane activation as shown by a multi-technique approach which couples *in-situ* DRIFTS and *operando* soft X-rays NEXAFS spectroscopies.

Experimental/methodology. A series of catalysts with a CeO_2 loading between 20% and 80% wt. were prepared by mixing CeO_2 and CuO in a ball mill and compared with samples prepared by impregnation. Materials were characterized by means of XRD, TPR, BET, SEM, *in-situ* DRIFTS and *operando* NEXAFS. Theoretical calculations were performed in order to confirm the experimental results.

Results and discussion. The *operando* NEXAFS experiments performed on the CeO_2/CuO milled samples has shown the formation of Cu^{+} and the disappearence of Ce^{3+} during the activation phase at 300°C under inert conditions, thus demonstrating a promotion of charge tranfer between Ce^{3+} and Cu^{2+}. Moreover, in contrast to the behaviour of impregnated samples and to the pure CuO and CeO_2, in the milled samples activation of methane at the relatively low temperature of 250°C occurs, as evidenced by formaton of methoxy and formate species upon exposure to a a 10%CH_4/He atmosphere. The intensity of the Cu^{+} feature increased during the exposition to methane atmosphere, thus indicating the pivotal role of Cu^{+} atoms in its activation. During the exposition in pure He the features related to this copper species remained stable, and disappeared following exposition in 5%O_2/He atmosphere, in agreement with the fate of methoxy and formates observed by DRIFTS. Traces of the partial oxidation products (formaldehyde and methanol) were observed in addition to CO_2 and water by monitoring reaction products during the *operando* NEXAFS. Repeated cycles of CH_4/He/O_2 returned the same results confirming a reversible behaviour. Theoretical calculations support the experimental evidence of a charge transfer between Ce^{3+} and Cu^{2+} and show that oxygen vacancies are easily created at the interface between the two oxides. Moreover, methane activation through C-H bond cleavage at the interface is considerably facilitated compared to the two isolated parent oxides, in agreement with DRIFT measurements.

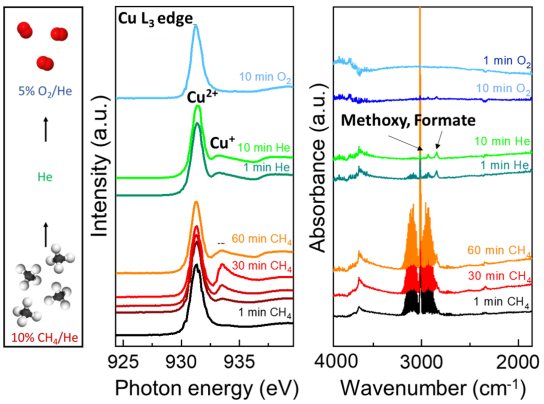

Figure 1: evolution of the Cu L_3 adsorption edge (left) upon exposure to methane (red), inert (green) and oxygen (blue) and corresponding DRIFT spectra (right).

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Exploring ZSM-5/alumina Shaped Objects with X-ray Diffraction Computed Tomography

I. Capel Berdiell[1*], D. Wragg[2], T. Cordero-Lanzac[1], N. Haaber-Junge[1], P. Beato[3], L. F. Lundegaard[3], G. Vaughan[4], M. Di Michel[4], L. P. Nogueira[5] and S. Svelle[1]

[1] *Center for Materials Science and Nanotechnology (SMN), University of Oslo, Oslo, Norway*
[2] *Institute for Energy Technology, Kjeller, Norway*
[3] *Haldor Topsøe A/S, Lyngby, Denmark*
[4] *ESRF-The European Synchrotron, Grenoble, France*
[5] *Department of Biomaterials and Oral Research Laboratory, University of Oslo, 0317 Oslo, Norway*
[*] *izarc@uio.no*

Keywords: XRD, Tomography, MTH, Shaped objects

Introduction. Most frequently the academic sector studies pure catalyst powders, while in industry catalysts are usually formulated into objects whose composition, size and shape are optimized for a given process and reactor. Extrudates in cylindrical (Fig 1a) or other shapes are common, but spray-dried particles [1] (Fig 1b) can also be used. We recently used *operando* X-ray diffraction computed tomography (XRDCT) to image cylindrical extrudates using crystal structure parameters [2-3], showing how radial coking gradients develop in such objects during MTH [4]. In this work, we use *operando* XRDCT to follow the coke burning process during temperature-programmed oxidation (TPO) of the coked cylindrical extrudates.



Figure 1: *a*) Photo of cylindrical extrudates. *b*) SEM picture of spray dried spheres

Results and discussion. Fig 2a shows the evolution of radial coke gradients with temperature during TPO, which suggests that coke is removed from inside out. XRDCT with a spatial resolution of 300 nm on coked spray dried spheres (Fig 2b), show an even spread of coke through the whole object, suggesting that there are no diffusion limitations within the small spheres and consequently, that the latter shaping process could be worthwhile. Nano-CT imaging of the spheres (Fig 2c) at the same spatial resolution confirm the distribution of bubbles and alumina support crystallites in the walls of the spheres in 3D.

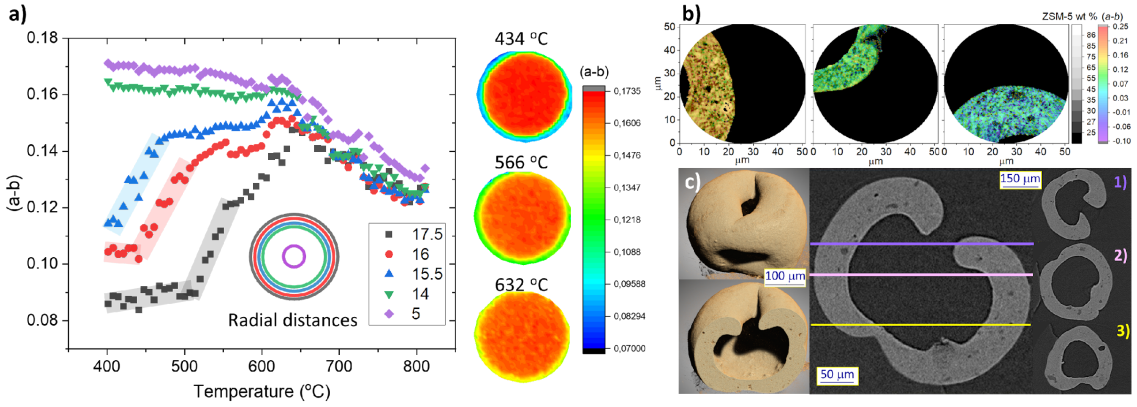

Figure 2: *a*) XRDCT slices of a cylindrical extrudate at 3 temperatures during TPO and *(a-b)* descriptor evolution at different radial distances averaged. *b*) coke distribution in the sphere walls at 0.3 µm^2/pixel resolution for fresh, partially and fully deactivated spheres. *c*) Nano-CT 3D reconstruction of the sphere showing voids and density variations in the walls

Acknowledgments
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Crystallite Size Dependent Oxidation of Ni Catalysts Revealed by *in situ* Magnetometry

D. de Oliveira[1], N. Fischer[1], M. Higham[2], C.R.C. Catlow[2] and M. Claeys[1,*]

[1]*Catalysis Institute, University of Cape Town, Cape Town, South Africa*
[2]*School of Chemistry, Cardiff University, Cardiff, United Kingdom*
michael.claeys@uct.ac.za

Introduction. Nickel catalysts are known for their industrial use in both steam reforming and methanation reactions[1]. In addition to being active for these two reactions, Ni is also used in the CO_2 methanation reaction, which has gathered much recent interest due to the global climate crisis and need to lower CO_2 emissions[2]. CO_2 methanation has the potential to act as a means of energy storage of renewable forms of energy, which have an intermittent supply. In these reactions, the catalysts are exposed to the presence of steam, high temperatures and high pressures. Deactivation typically occurs *via* sintering and carbon deposition, however some studies have also reported small amounts of oxidation[1]. This observation is particularly interesting, since the oxidation of nickel is not thermodynamically feasible at the conditions relevant to these processes. This observation is thought to be due to the size dependent oxidation of nano-crystallites[3]. This work investigates the size dependent oxidation of a model nickel catalyst system, using an *in situ* magnetometer.

Experimental/methodology., The catalysts were prepared by homogeneous deposition precipitation. These were reduced at both 400 °C and 700 °C to produce the nanoparticles with 2 different sizes. The in house developed UCT *in situ* magnetometer[4] was used to conduct the oxidation testing experiments, which was carried out at 250 °C under a simulated gas environment of H_2O/H_2 while the magnetic measurements were recorded. The P_{H2O}/P_{H2} was varied from 0 to 400 to induce the oxidation of the catalysts, with each condition being held at 1 hour.

Results and discussion. The samples reduced at 400 °C and 700 °C had average sizes of 4 nm and 8 nm respectively, with nanoparticles distributed over the support (Figure 1A-B) and minimal overlap of size distributions (Figure 1C). Since Ni is the only magnetic phase in this system, a decrease in the magnetization indicates the oxidation of Ni to a non-magnetic phase (such as NiO or a Ni-based support compound). Figure 1D shows that the smaller nanoparticle size is more susceptible to oxidation, with the 3.5 nm sample oxidizing significantly at a P_{H2O}/P_{H2} of 30, while the 7.5 nm only oxidized at ratio of 200. These results were then validated against thermodynamic calculations for the size dependent oxidation, which showed good agreement with the experimental results, providing direct evidence for the size dependent oxidation behaviour of Ni nanoparticles.

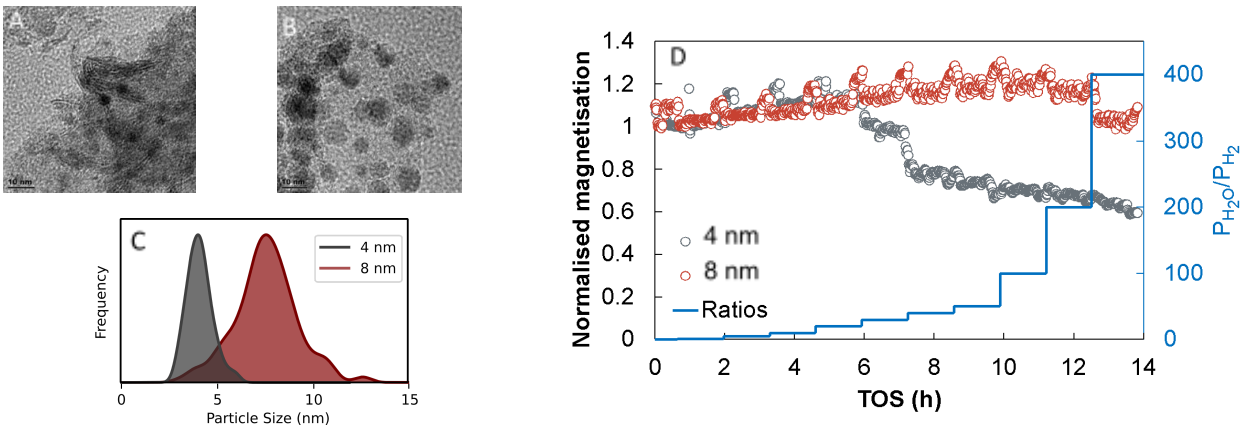

Figure 1: A) TEM images of 4 nm sample B) 8 nm sample and C) size distriubtions. D) Oxidation testing results from magnetometry experiments.

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Support Effects on the Preferential Oxidation of Carbon Monoxide over Co_3O_4 Nanoparticles Studied *In Situ*

T.M. Nyathi[1]*, M.I. Fadlalla[1], N. Fischer[1], A.P.E. York[2], E.J. Olivier[3], E.K. Gibson[4], P.P. Wells[5], M. Claeys[1]*

[1]*Department of Chemical Engineering, University of Cape Town, Rondebosch 7700, South Africa*
[2]*Johnson Matthey Technology Centre, Sonning Common, Reading RG4 9NH, United Kingdom*
[3]*Physics Department, Nelson Mandela University, Gqeberha 6031, South Africa*
[4]*School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, United Kingdom*
[5]*School of Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom*
**Corresponding authors: thulani.nyathi@uct.ac.za and michael.claeys@uct.ac.za*

Keywords: Fuel Cell Hydrogen, CO-PrOx, Co_3O_4 Nanoparticles, Support Effects, *In Situ* Characterisation

Introduction. The preferential oxidation of CO (CO-PrOx) to CO_2 remains the most viable catalytic process for removing the trace poisonous amounts of CO (0.5 – 2%) in the H_2-rich reformate gas mixture before being fed into polymer electrolyte membrane fuel cells. Cobalt(II, III) oxide (Co_3O_4) is a promising catalyst for CO-PrOx but often undergoes deactivation *via* reduction to Co^0 at high reaction temperatures (>200 °C) because of the high amounts of H_2 (40 – 75%) in the CO-PrOx feed [1]. The presence of Co^0 causes an undesired change in the conversion pathway of CO from oxidation to hydrogenation, thus forming CH_4 instead of CO_2. Therefore, this (already published) study [1] aimed at anchoring Co_3O_4 nanoparticles (NPs) on various metal oxide support materials to evaluate their effect on the phase stability as well as the CO oxidation activity and selectivity of Co_3O_4 NPs under model (or dry) CO-PrOx conditions.

Experimental. Supported Co_3O_4 catalysts (with 10 wt.-% Co_3O_4) were prepared *via* the incipient wetness impregnation of the supports ZrO_2, TiO_2-rutile, TiO_2-anatase, and Al_2O_3 with aqueous $Co(NO_3)_2.6H_2O$. *In situ* catalyst characterisation and evaluation during CO-PrOx involved instruments developed at the University of Cape Town (South Africa), namely, a low-frequency vibration sample magnetometer [2] and PXRD capillary-based reaction cell [3], between 50 and 450 °C at atmospheric pressure, using a GHSV of 60000 $mL/g_{Co3O4}/h$. The reaction feed composed of CO (1%), O_2 (1%), H_2 (50%), and N_2 (48%).

Results and discussion. The Co_3O_4/ZrO_2 catalyst achieved the highest CO_2 yield (91.5%), followed by Co_3O_4/TiO_2-rutile (60.7%), Co_3O_4/TiO_2-anatase (51.5%), and Co_3O_4/Al_2O_3 (26.6%) at 200 °C. However, the degree of reduction (DOR) of Co_3O_4 to Co^0 was highest on ZrO_2 (100.0%), followed by TiO_2-rutile (85.9%), TiO_2-anatase (76.4%), and Al_2O_3 (16.2%) at 450 °C. In the spent Co_3O_4/TiO_2-anatase catalyst only, TiO_x-encapsulated CoO_x NPs were observed *via* STEM analysis. Undesired CH_4 production occurred over the Co^0 NPs formed on ZrO_2 (100%), TiO_2-rutile (73.7%), and Al_2O_3 (57.8%), while no CH_4 was formed over the Co^0 NPs on TiO_2-anatase possibly due to their encapsulation by TiO_x species. The observed trends in terms of CO_2 yields and DOR can be attributed to the nature of the nanoparticle-support interactions (NPSI) in each supported catalyst. For example, the weak NPSI in Co_3O_4/ZrO_2 resulted in high CO oxidation activity *via* the Mars-van Krevelen mechanism, which requires the catalyst surface to be easily reducible and re-oxidisable [4]. However, these weak NPSI also led to the undesired high DOR and CH_4 yield reached at 450 °C. On the other hand, the strong NPSI in Co_3O_4/Al_2O_3 caused the catalyst to be the least reducible and least CO oxidation active.

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Studies of the structure-transport relationships in gamma alumina catalytic supports using NMR cryodiffusometry

S. Collins[1,2*], H. Williams[1], C. Parmenter[1], C. Vallée[2], T. Chevalier[2], D. Lofficial[2], S. Rigby[1]

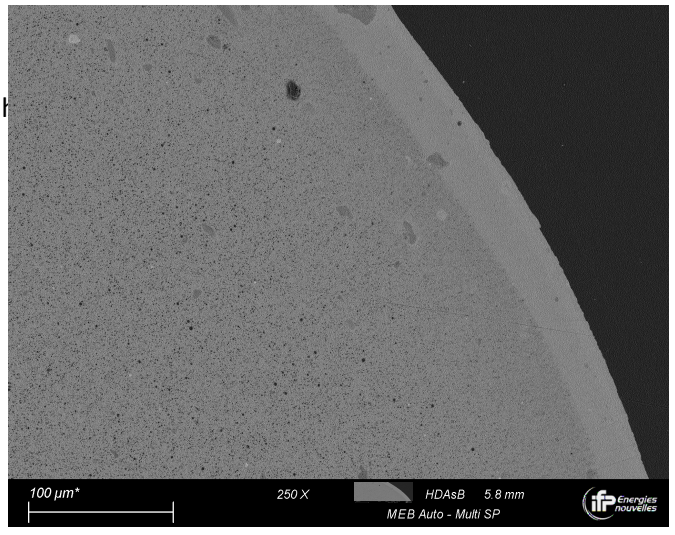
[1] *University of Nottingham, Nottingham, United Kingdom*
[2] *IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France*
[*] *Corresponding Author's E-mail address: enysmc@nottingham.ac.uk*

Keywords: Catalytic support, NMR cryoporometry, Diffusion, Porous media, Tortuosity

Introduction. Many heterogeneously-catalysed industrial processes are diffusion-limited. In addition, many processes suffer from solids deposition, liquid condensation, and/or sintering of the catalyst, such that the pellet structure evolves during usage. In many processes, the harsh thermochemical conditions mean that only amorphous materials can be used, since delicate controlled pore-size materials rapidly degrade. Hence, there is a need to understand how the random pore structure influences mass transport, to the extent that the tortuosity factor can be predicted. However, the typically complex, hierarchical nature of pellet structure often means that a so-called "brute force" approach is beyond the reach of current computing power, and some selection of the key structural features to incorporate in a model is necessary. In this work, the combination of NMR cryoporometry and pulsed-field gradient (PFG) NMR, known as cryodiffusometry, has been used to investigate the relative importance of different aspects of the void space, and various bins within the pore size distribution, to mass transport rates in bimodal amorphous gamma alumina support pellets, with different degrees of controlled macroporosity.

Experimental/methodology. NMR cryodiffusometry experiments, using water as the probe fluid, were performed using both boundary and scanning, and both melting and freezing curves, to comprehensively dissect the void space and isolate key features that determine mass transport rates. These experiments were coupled with complementary DSC thermoporometry to coroborate the cryoporometry results, and also FEG-SEM and FIB-SEM experiments to aid the interpretation of the NMR data.

Results and discussion. The shapes of the hysteresis loops in cryoporometry scanning experiments initiated from sample states, wherein the macroporosity was still frozen, have indicated differences in the incidence and pervasiveness of the macroporosity, to compare with statistics from the imaging data. The data was used to assess the contribution of the macroporosity to mass transfer rates, and also explore the rind effect detected in microscopy experiments, illustrated in Figure 1. The cryodiffusometry experiments have also been used to test for blinding of the interface between macropore and mesopore networks, that would greatly hinder Knudsen regime gas-phase transfer between the two [1].



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I am grateful to E. Jolimaitre for her guidance and support in her time as my IFPEN supervisor during 2022.

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Investigating the effect of Cu on dealumination in CHA zeolites

V. Saltão[1,2*], V. Crocellà[2], S. Bordiga[2], G. Berlier[2]

[1]Umicore AG & Co KG, Automot Catalysis Div, Res & Dev, Hanau, Germany
[2]*Department of Chemistry, and NIS Centre, Università di Torino, Via P. Giuria 7 – 10125 Italy*
[*]*Corresponding Author's E-mail address: vascoantnio.correiasalto@unito.it*

Keywords: NH_3-SCR, chabazite, Cu, hydrothermal aging, dealumination, IR spectroscopy

Introduction: NO_X selective catalytic reduction by NH_3 (NH_3-SCR) is commonly used to reduce emissions of polluting NO_X from combustion engines exhaust gases. Of all known catalysts for NH_3-SCR, Cu-zeolites, and specifically Cu-CHA, present the best hydrothermal stability and performance in the 180-300 °C range, maintaining it for higher temperatures [1,2]. This makes Cu-CHA an important NH_3-SCR catalyst, as increasing fuel efficiency drives down combustion temperatures [2]. However, repeated exposure to the high temperatures of exhaust systems in the presence of water, may cause dealumination [3]. This deactivates the catalyst, since the Cu active sites are stabilized by the negative charge induced on the framework by Al atoms. This project aims to study the structure of Al and Cu after dealumination, and how differently dealumination affects zeolites with different Cu and Al contents.

Experimental/methodology: Fresh and hydrothermally treated (650 °C for 100 hours) Cu-CHA catalysts with different Si/Al ratio (6.7 and 15) and Cu content (0, 3.2 and 0.8 wt%) were characterized about their structural and textural properties and by in situ IR spectroscopy .

Results: XRD and gas-volumetric measurements indicate that after aging the crystallinity and textural properties of the samples are maintained. However, IR spectra collected in N_2 flow at 350 °C highlight that the intensity of the Brønsted sites signals (3600 and 3575 cm^{-1}) decreases after aging, whereas the intensity of the partial extraframework AlOH (3650 cm^{-1}) slightly increases in both Cu-CHA samples (Figure 1), indicating dealumination. Also, the Si/Al = 6.7 aged sample presents a new signal at 3624 cm^{-1}, which we attribute to newly formed Brønsted sites as a result of local structure damaging from dealumination. Further studies are ongoing to investigate the nature of the defective sites and the effect of dealumination on the Cu sites active in NH_3-SCR reaction.

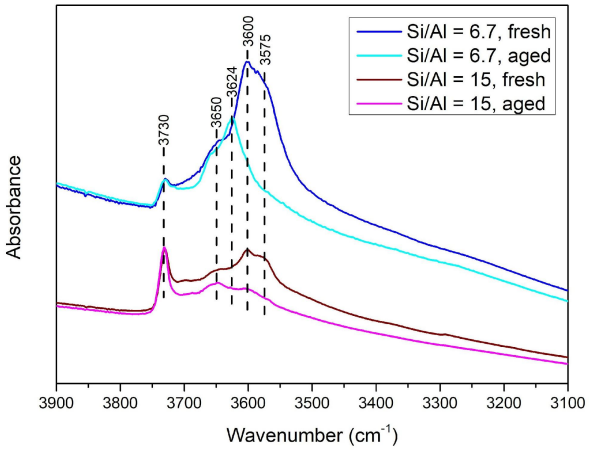

Figure 1 - IR spectra of OH stretching region of fresh and aged Cu-CHA samples with 3.2 Cu wt% at 350 °C in N_2 flow

***Acknowledgments**: The authors acknowledge the support of the European Union's Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement no. 955839 (CHASS).*

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Operando DRIFTS-MES study of CO-Oxidation over $LaFe_{1-x}Co_xO_3$ catalysts

Nicolas Cosanne[1], Maik Dreyer[2], Sharif Najafishirtari[1], Malte Behrens[1*]
[1]*Christian-Albrechts-Universität zu Kiel, 24118 Kiel*
[2]*University of Duisburg-Essen, 45141 Essen*
[*]*mbehrens@ac.uni-kiel.de*

Keywords: CO-Oxidation, Perovskites, Cobalt, DRIFTs, MES, Steady State Catalysis

Introduction. Perovskites are an interesting alternative to noble-metal catalysts, offering high flexibility in their composition and showing high reactivity in different reactions.[1-3] In this work, we focus on the most interesting $LaFe_{1-x}Co_xO_3$ catalysts (x=0 and x=0.25) from a previous study in our group.[1] The samples were studied via steady-state gas-phase analysis to estimate activation energies. To have a more in-depth look into the reaction mechanism, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) combined with modulation-excitation-spectroscopy (MES) was employed.

Experimental/methodology. The precursors were synthesized via co-precipitation in an automated lab reactor (*OptiMax 1001, Mettler Toledo*) at 10 °C and a pH of 9.5. They were thermally decomposed to the perovskites in a muffle furnace at 600 °C under air atmosphere. Steady State CO-oxidation experiments were carried out in a home-build setup with a feed gas of 2% CO and 1% O_2 in nitrogen as a carrier gas over 100 mg of sieved catalyst (250-355 µm). Following a temperature programmed oxidation (TPO) at 250 °C, data was recorded in six steps from 100-250 °C for 2 hours per temperature. DRIFTS-MES was recorded on a *ThermoFisher Nicolet™ iS20* FTIR spectrometer with the *Praying Mantis™* (*Harrick Scientific Products Inc.*) accessory and a nitrogen cooled MCT-detector, coupled with *OMNISTAR™ GSD 320* mass spectrometer (MS) at four different temperatures per catalyst.

Results and discussion. The steady state studies showed a higher conversion and reaction rate for the Co-containing sample, as was expected from our previous study (Figure 1 a)).[1] The resulting activation energy of CO was also lower on that sample, supporting the findings of the transient experiments. The higher CO_2 rate was also observed on the Co-containing sample in the DRIFTS-MES experiments on the MS, which was corroborated by the CO_2 band in the IR spectra. Further analysis of the carbonate region showed interesting trends on the formation of different bands at different temperatures. Shoulders at 1569 cm^{-1} and at 1354 cm^{-1} are more pronounced at higher temperatures. Furthermore, a band at 1386 cm^{-1} is seen predominantly on the Co-containing catalyst at lower temperatures. Phase delay analysis further revealed a faster formation of the carbonates at higher temperatures on the sample without Co, while the Co-containing sample showed only minor changes in the phase delay for all recorded species. Another point of interest is the hydroxide region, which is not visible on the Co-containing sample, but on the Co-free sample is clearly visible, especially at 200 °C. All these finding indicate a possible different reaction mechanism with different transition states, which is under further investigation through DFT-based calculations.

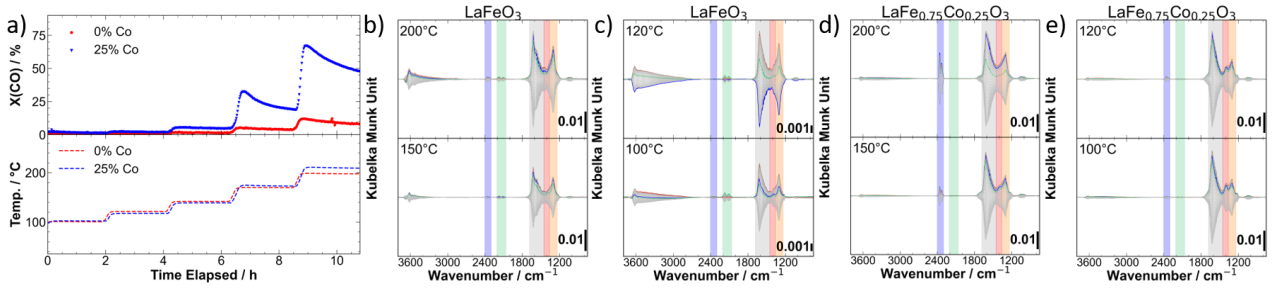

Figure 1: a) CO consumption rate and temperatures during steady state experiments; MES spectra at 200, 150, 120 and 100 °C for the Co-free (b and c) and Co-containing (d and e) samples.

Acknowledgments
This work was funded by the DFG (388390466, TRR 247) within the projects C1, A1 and A8.

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Investigations of the Effect of H_2 in CO Oxidation over Ceria Catalysts

A. Davó-Quiñonero[1,2]*, S. López-Rodríguez[1], C. Chaparro-Garnica[1], I. Martín-García[3], E. Bailón-García[1], D. Lozano-Castelló[1] , A. Bueno-López[1], M. García-Melchor[2]

[1]*Inorganic Chemistry Department, University of Alicante, Alicante, Spain*
[2]*School of Chemistry and AMBER Research Centres, Trinity College Dublin, Dublin, Ireland*
[3]*Organic Chemistry Department, University of Alicante, Alicante, Spain*
*arantxa.davo@ua.es

Keywords: nano-shaped ceria, CO oxidation, CO-PROX, DFT calculations, reaction mechanism, DRIFTS

Introduction. Ceria-based materials have been extensively used as CO oxidation catalysts due to their unique redox features [1]. A particular niche of this application is the preferential CO oxidation (CO-PROX), which is the preferred catalytic strategy towards the removal of CO impurities from H_2 reformate streams. As an intrinsic characteristic of CO-PROX, CO selectivity drops with temperature, and the steepness of the fall mainly depends on the difference between the CO and H_2 oxidation reaction onsets. Interestingly, although there are comprehensive reports addressing the competitive nature between CO and H_2 oxidation reactions on CeO_2 -based catalysts, the underlying interaction of hydrogen with CO oxidation is still an unresolved question. Herein, we present a theoretical description of the CO-PROX reaction mechanism within the CO selective regime on the low-index CeO_2(111), CeO_2(110) and CeO_2(100) surfaces by means of periodic density functional theory (DFT) calculations combined with an experimental spectroscopic study.

Experimental/methodology. Polycrystalline ceria was prepared by simple nitrate calcination while CeO_2 cubes and CeO_2 rods were synthesized by adapting reported hydrothermal methodologies [2]. CO-PROX ($CO+O_2+H_2$) and CO-TOX ($CO+O_2$) operando DRIFTS experiments were performed to monitor surface species during the reaction. DFT(+U) calculations were performed with the VASP package implementing the Perdew–Burke–Ernzenhof (PBE) exchange correlation functional and projector augmented wave (PAW) potentials with a kinetic cut-off energy of 500 eV. Gibbs adsorption energies were computed and transition states (TS) for the relevant steps were located by means of the climbing image nudge elastic band method (CI-NEB).

Results and discussion. The low-index CeO_2 surfaces display different features that have a momentous impact on their catalytic behavior. In CO oxidation, the (110) termination of ceria is the most favorable due to a facile oxygen vacancy formation owing to its open structure**.** Our results reveal that hydrogen improves the interaction between CO and ceria, although the reaction onset is not lowered compared to the H2-free environment due to the lack of available O surface sites, which become hydroxylated in the presence of H_2. The carbonate to bicarbonate route is feasible on the (110) and (100) surfaces, but not on the main (111) facet, and only provided the reaction occurs at low temperatures [3].

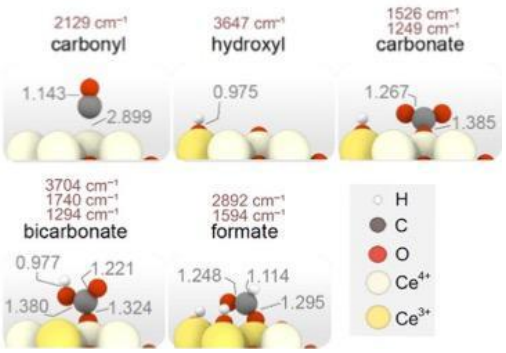

Figure. Adsorption modes for CO, CO_2 and H_2 on stoichiometric CeO_2(111), vibrational frequencies and bonding distances (in Å).

Acknowledgments. *Spanish Ministry of Science and Innovation (PID2019-105960RB-C22, RYC2021-034791-I, TED2021-129216B-I00, PDC2022-133839-C22), Generalitat Valenciana (CIPROM/2021/74, MFA/2022/036) and Irish Centre for High-End Computing (ICHEC).*

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Structural, textural and functional properties of supported Cu- and Zn-containing catalysts for hydrogenation of CO_2

A. Proszowska[1], Y. Vitushynska[1], P. Rybowicz[1], P. Legutko[1], M. Michalik[2], A. Adamski[1*]

[1]*Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, PL 30-387 Krakow*
[2]*Jagiellonian University, Faculty of Geography and Geology, Gronstajowa 3a, PL 30-387 Krakow*
[*]*a.adamski@uj.edu.pl*

Introduction. Even if rather demanding, due to the high therodynamic stability of CO_2 molecules, catalytic valorization of CO_2 is important from both environmental and technological viewpoints. On one hand, it is crucial for efficient reduction of CO_2 emissions, yet CO_2 conversion can also provide such important market products, like e.g. synthesis gas, hydrogen or methanol. In this paper, our attention is focused on supported copper- and zinc-containing catalysts for CO_2 hydrogenation to methanol. For at least a decade, copper-based systems have been known to be active in this reaction. Commercial gamma alumina and cenospheres (Cen) from fly ashes have been tested as catalytic supports. The use of the latter support is an emblematic example of a circular-economy-based approach at designing catalytic materials. Our goal was to explain the effect of copper and zinc concentrations on structural, textural and functional parameters which can control the catalytic properties of the supported systems. Additionally, the effect of nature of both active phase and support has been understood and elucidated in more detail.

Experimental/methodology. Two series of γ-Al_2O_3- or cenosphere-supported catalysts, containing copper (0.5-10.0 mol.%) or a combination of copper and zinc (0.2-4.0 mol.%) as active components have been synthesized via modfied impregnation method. All samples have been calcined in air at 400°C for 4h. Commercial cenospheres of 300 mm in diameter have been used. The studied samples have been structurally (XRF, XRD, RS), texturally (SEM/EDS, porosimetry) and functionally (RS, DRIFT and UV/Vis-DR) characterized.

Results and discussion. The obtained results clearly suggest that for a given copper content, calcination temperature, nature of the support and the presence of zinc additives can influence the dispersion and speciation of copper sites exposed on catalyst surface. The same parameters can thus be decisive for both catalytic performance and stability of the studied systems. Cenospheres used as one of our catalytic supports distinctly favor stabilization of nanocrystalline CuO and ZnO 3D entities on catalyst surfaces, whereas γ-Al_2O_3 support facilitates higher dispersion of the deposited active components. In the latter case, only for copper contents above 10 mol. % the appearance of the CuO forms was confirmed. Regardless of loadings, heterogeneity of surface hydroxyls stabilized on cenosphere-supported catalysts was distinctly stronger in comparison to that observed for γ-Al_2O_3-supported samples. The presence of octahedral CuO_6 surface centers was confirmed for almost all investigated samples. Larger CuO_x surface clusters were stabilized on catalyst surfaces at higher copper loadings. The addition of zinc additives modified surface architecture dependently on its loading and on the initial copper content.

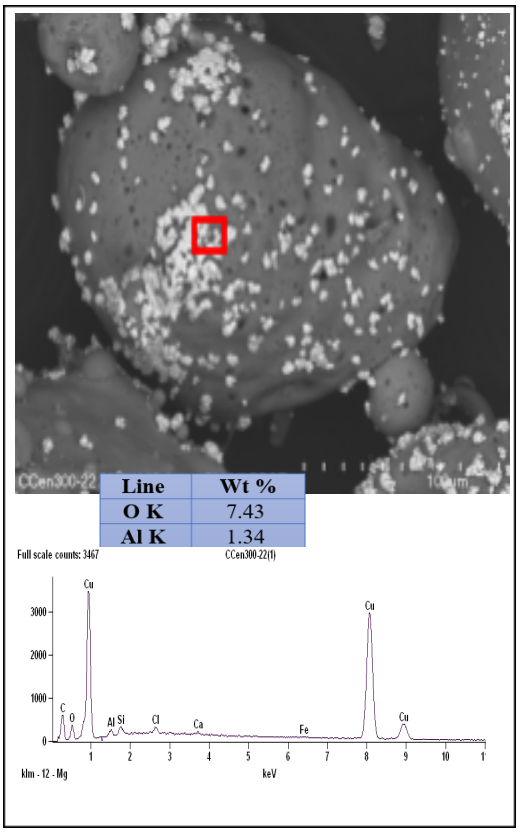

Fig. A representative SEM image of Cu/Cen sample containing 5 mol. % of Cu with EDS analysis of the marked area.

Kinetics of hydrogen release in mono- and bimetallic PdX nanoparticles probed by QEXAFS and synchrotron XRD

D.E. Doronkin[1,2*], T.J. Eldridge[1], S. Wang[2], S. Behrens[2], J.-D. Grunwaldt[1,2]

[1]*Institute of Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Engesserstraße 20, 76131, Karlsruhe, Germany;* [2]*Institute of Catalysis Research and Technology, Kalrsruhe Institute of Technology, Hermann-von Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

[*]*dmitry.doronkin@kit.edu*

Introduction. Supported mono- and bimetallic Pd-based catalysts are the catalysts of choice for selective hydrogenation reactions such as direct hydrogen peroxide [1] and semi-hydrogenation of alkynes [2]. Under typical hydrogenation conditions (relatively low temperatures and high partial pressures of H_2) Pd nanoparticles are present as surface and bulk hydrides, and it is the hydride H which is believed to be the hydrogenating agent. The nature of hydride H is believed to define the hydrogenation pathways with surface hydrogen (typically found in α-PdH_x) being the selective "mild" hydrogenating species and bulk H (from β-PdH_x) favoring total (over-)hydrogenation reactions [2]. Alloying Pd with a second metal can be used to alter its H uptake capacity and therefore activity and selectivity of the resulting catalysts [3]. However, so far studies of hydride formation and decomposition of mono- and bimetallic Pd nanoparticle based catalysts were performed in the steady-state regime and it is still unclear how tuning the Pd nanoparticle size and shape as well as alloying Pd with other metals affects kinetics and the mechanism of hydrogen uptake and release including transformations between Pd metal, α-PdH_x, and β-PdH_x.

Experimental/methodology. A combination of quick scanning X-ray absorption spectroscopy (QEXAFS) and synchrotron XRD allowed probing realistic supported Pd and PdX (where X = In, Sn, Zn, Ga etc., approx. 6 wt% total metal loading on TiO_2 P25) hydogenation catalysts [4] with subsecond time resolution during fast switching of the gas atmosphere between pure H_2 and pure He at 298 K and 1 bar. A standard quartz capillary (2 mm o.d., 0.02 mm wall thickness) was used as an in situ cell with a plug flow geometry. Complimentarity of XANES/EXAFS (sensitive to both surface and bulk hydrides) and XRD (sensitive only to bulk hydrides) allowed indirect probing of H in the bulk and in the subsurface regions of Pd(X) nanocrystals.

Results and discussion. Combination of XAS and XRD with subsecond time resolution allowed establishing a multi-step pathway of hydrogen release from the surface and the bulk of Pd(X) nanoparticles which start with gradual β-PdH_x lattice contraction and followed by stepwise abrupt restructuring to α-PdH_x and Pd metal structures (indistinguishable by XRD, Fig. 1) with the corresponding rates obtaineble from QEXAFS (not shown). Changes in Pd particle size and shape as well as alloying Pd with other metals directly influence both the amount of stored hydrogen and kinetics of its release.

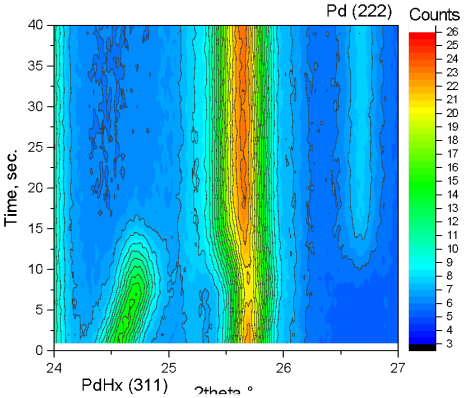

Figure 1. Temporal evolution of Pd/TiO_2 XRD patterns after switching from H_2 to He atmosphere.

Acknowledgments

We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at PETRA III, and we would like to thank Dr. Vadim Murzin (BU Wuppertal), Dr. Benjamin Bornmann (BU Wuppertal), and Dr. Wolfgang Caliebe (DESY) for assistance in using beamline P64.

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Operando XAS Study of Pd species during H_2-SCR of NOx

Thomas J. Eldridge, Michael Borchers, Patrick Lott, Dmitry E. Doronkin, Olaf Deutschmann, Jan-Dierk Grunwaldt

Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Keywords: H_2-SCR, Operando, XAS

Introduction. Among strategies for reducing engine-out emissions, hydrogen has been investigated for use in combustion engines. For such applications carbon emissions are negligible, however, NOx still forms as a pollutant. In this case, selective catalytic reduction (SCR) of NOx using H_2 is a promising candidate. While NH_3 is commonly used as a reducing agent in SCR of NOx, H_2 shows higher levels of activity relative to NH_3 at lower temperatures and is convenient due to the direct availability from the fuel tank. However, a challenge of H_2-SCR is combating the competitive direct oxidation of H_2 to H_2O, which becomes the favored reaction pathway at high temperatures.[1] Additionally, besides direct H_2-oxidation, several reactions are simultaneously occurring over the catalysts bed, including NH_3 formation and subsequently NH_3-SCR, leading to gradients in reaction product concentrations and in catalyst structure. In this context, our study focuses on the indentification of the the different H_2-SCR stages along a catalyst bed by means of spatially resolved X-ray absorption spectroscopy measurements.

Experimental/methodology. A 1 wt.% Pd/5%V_2O_5/20%TiO_2-Al_2O_3 catalyst, previously investigated in our laboratories,[1] and several Pd containing zeolites samples were investigatedby QEXAFS measurements (DESY P64 beamline, PETRA III) under *operando* H_2-SCR conditions at multiple spatial positions along the catalyst bed, in order to study the formation and decomposition of oxides, hydrides, and nitrides expected to form on Pd-nanoparticles under H_2-SCR conditions.[2-4]

Results and discussion. Among the findings, the reduction of Pd species was observed for the 1 wt.% Pd/5%V_2O_5/20%TiO_2-Al_2O_3 catalyst during the H_2-SCR reaction at temperatures between 150 and 225 °C., according to linear combination fitting of XANES spectra, as shown in Figure 1. The corresponding and gradual increase in H_2 conversion across the same temperature range, as indicated by the light-off curve in Figure 1 (left), suggests that Pd reduces shortly before H_2 becomes active in SCR, which is in good accordance with previous observations [1]. Rapid oxidation of Pd occurs as NO converts and H_2 is consumed.

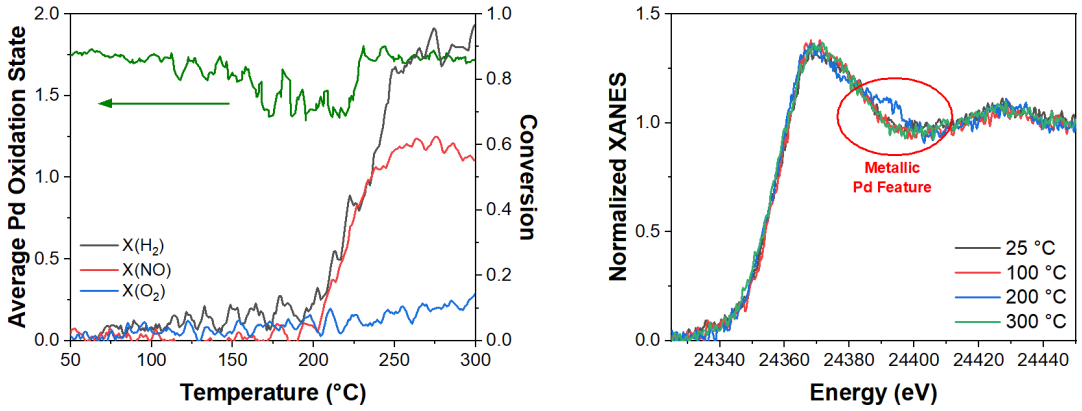

Figure 1: (left) ratio of oxidized Pd in a 1 wt.% Pd/5%V_2O_5/20%TiO_2-Al_2O_3 catalyst and corresponding conversions of H_2, NO, and O_2 as a function of temperature; (right) corresponding QEXAFS spectra at the Pd K-edge at different temperatures; 50 mL/min flow of 1000 ppm NO, 5000 ppm H_2, and 10% O_2 (He balance)

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NOTOS beamline at ALBA Synchrotron: new tools for catalyst characterization under *operando* conditions

C. Escudero[1*], G. Agostini[1], O. Vallcorba[1], J. Prat[1], D. Heinis[1], Á. Baucells[1], J. R. García[1], R. Homs[1], N. Serra[1], J. Nicolàs[1]

[1]*ALBA Synchrotron Light Source, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallès, Barcelona, Spain*
[*]*cescudero@cells.es*

Keywords: Operando, Catalysis, X-Ray Absorption Spectroscopy, X-Ray Diffraction

Introduction. NOTOS [1] is the last beamline from the ALBA Synchrotron Light Source open to external users which started operation in April 2022. This beamline, co-funded by the European Regional Development Fund (ERDF) within the pluri-regional operational program of Spain, is devoted to XAS, XRD, and metrology applications in the energy range of 4.5 – 30 keV with the capability to perform XAS and XRD investigations in a quasi-simultaneous way. NOTOS, as a new tool open for the scientific community, allows to study the electronic structure, short- and long-range order by XAS and XRD within a wide range of scientific disciplines: chemistry, catalysis, energy science, nanomaterials, condensed matter and environmental science. In particular, NOTOS has been further developed to focus on *in situ* and *operando* measurements on heterogeneous catalysis and electrochemistry.

Experimental/methodology. Two different stations are available (Fig.1A,B). The first one consists of a 2.0 x 0.8 m table open to perform metrology measurements and suitable to XAS investigation in transmission and fluorescence mode by means of three ion chambers and one 13-elements SDD detector respectively. This endstation is being commissioned and is open to future developments, depending on the needs identified together with the user community, but it basically offers a big space to adapt for example catalytic reactors from the users in an easy way. The second station is equipped with a two circle diffractometer and 10-channel Ge(111) analyzer detector for high resolution XRD and a position sensitive detector for powder diffraction (Mythen, 6 modules). In this case, XAS can also be performed in transmission and fluorescence configuration. For both endstations, a setup to dose gases (up to 11 gas lines) at controlled flow (different flow ranges < 50 mL/min per gas) and pressure (currently up to 20 bar) and fully integrated in the beamline control system has been built (Fig.1C).

Results and discussion. In this contribution, we will show the new *state-of-the-art* tools that NOTOS offers and that can be applied to foster catalysis research.

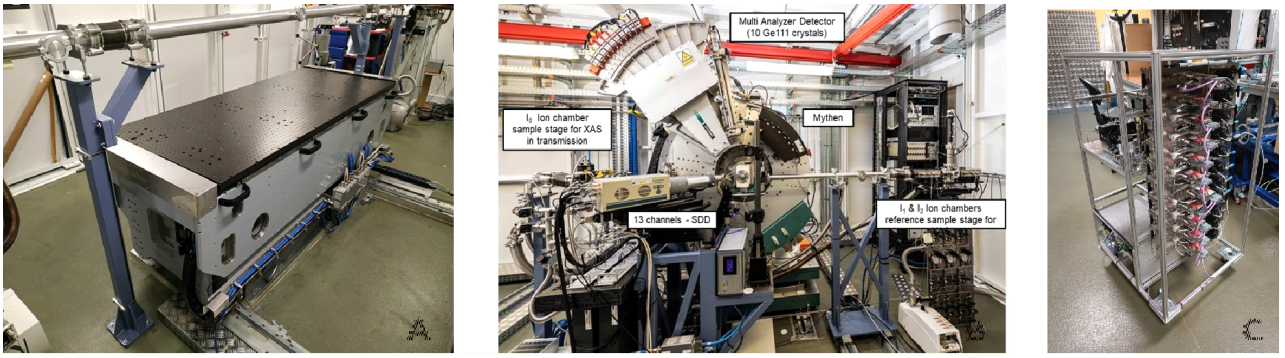

Fig.1 (A) Multipurpose endstation; **(B)** Powder Diffraction-XAS endstation; (C) Home-built fully integrated gas system

References

[1] BL-16 – NOTOS beamline, https://www.cells.es/en/beamlines/bl16-notos

Understanding the Impact of Reaction Conditions on Methanation Catalyst Structure and Performance using *in-situ* Total Scattering

B. Fahl[1*], F. Manzoni[1], F. Müller[1], M. Zobel[1]

[1]*Institute of Crystallography, RWTH Aachen University, Aachen, Germany*
[*]*Benjamin.Fahl@rwth-aachen.de*

Introduction.
In-situ total scattering enables real-time observation of catalyst structures during catalysis for improved catalyst design and performance. We apply this technique to study the effects of hydrogen dropouts, emulating the fluctuations found in renewable hydrogen feedstocks, to optimize the methanation reaction [1]. Using a heterogenous urea precipitation-based Ni@γ-Al_2O_3 catalyst we follow particle growth and further structural changes while simultaneously tracking activity and selectivity with mass spectrometry (MS).

Experimental/methodology.
The pair distribution function (PDF) is a technique used in high-energy X-ray total scattering experiments to determine the pairwise distances of atoms in a material. This information can be used to study the size, structure and morphology of nanoparticles on a support [2,3]. By utilizing sensitive, fast 2D detectors at synchrotron radiation sources sub-second time resolution can be achieved. Moreover, our flow cell design permits for a sample environment that closely represents laboratory-based catalytic reactions, that we coupled with MS directly at beamline ID15 at the ESRF using an X-ray energy of 65 keV.

Results and discussion.
Our study demonstrates the utility of the *in-situ* PDF technique coupled with MS for investigating catalytic reactions in real-time. We were able to capture detailed structural information about the reaction process over a 6-hour period, including 5 catalysis and 4 drop-out cycles, with a time resolution of 100 ms (Fig. 1). By simulating real-world conditions, such as hydrogen dropouts in solar-based hydrogen production, we were able to examine how these fluctuations impact particle growth and deactivation. Additionally, we observed ongoing structural changes in the catalyst during extended dropout conditions, evident in the increasing lattice parameter during dropouts, while the lattice parameter remained comparably constant throughout methanation. These findings highlight not only the impact of dynamic conditions, but also the significance of prolonged hydrogen absence on the catalyst structure and performance.

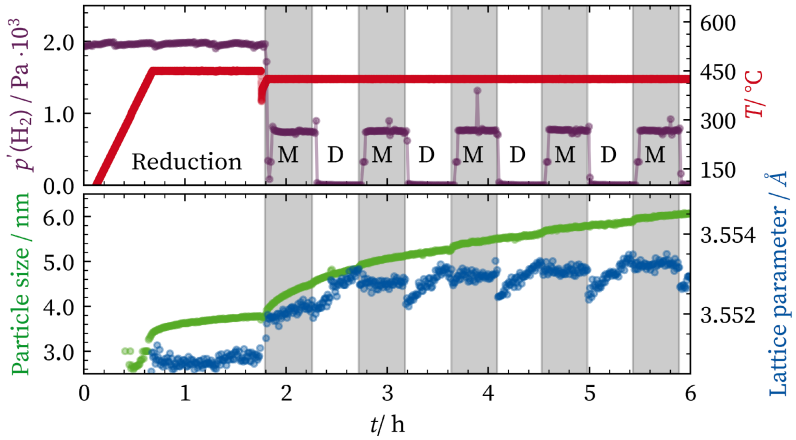

Fig. 1 Structural evolution of Ni@□-Al_2O_3 methanation catalyst during reduction and catalysis refined from *in-situ* total scattering experiments. Top: Experimental hydrogen partial pressure and temperature profile during reduction, methanation (M, with CO_2: H_2 = 4:1 in shaded areas) and hydrogen dropout (D) cycles. Bottom: Evolution of lattice parameter and particle size of Ni_{fcc} particles from PDF refinements.

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Synthesis and characterization of mixed metal NH_2-MIL-125 based metal-organic frameworks for use as catalysts

Leidy Figueroa-Quintero[1*], Javier Narciso[1], Enrique V. Ramos-Fernandez[1]

[1]*Instito Universitario de Materiales (IUMA), Inorganic Chemistry Department, University of Alicante, Alicante, Spain*

[*]*leidy.figueroa11@ua.es*

Introduction.

Metal-organic frameworks (MOFs) are a class of crystalline micro-mesoporous hybrid materials with an extended three-dimensional framework that have shown a wide variety of potential applications. MOFs have great potential as heterogeneous catalysts and photocatalysts [1],[2]. The so-called NH_2-MIL-125(Ti) structure has photocatalytic activity and a very high specific surface area, which makes it a promising material for various photocatalytic processes. However, to make it more versatile and applicable to different photocatalytic reactions, it is necessary to precisely tune its band gap and valence band position. To achieve this, we have developed a post-synthesis methodology in which part of the metal constituting the MOF (Ti) has been replaced by another metal M (M: Ce, Zr, Nb or Sc). In this way, we were able to modify the photocatalytic properties of the MOFs. The synthesised materials were tested in the photodegradation of dyes.

Experimental/methodology.

For the synthesis of the starting material the following procedure was carried out: in a mixture of DMF and methanol was put titanium isopropoxide and aminoterephthalic acid with constant stirring, the mixture was heated at 150˚C for 24h and the solid was separated by centrifugation, being this washed 2 times with DMF to remove the unreacted ligand and 2 times with methanol and finally the material was activated at 150˚C under vacuum for 12h. To perform the metal ion exchange, the metal M salt was placed in a DMF:methanol mixture, then the starting MOF was supended, heated at 80˚C for 3 days and washed with methanol in a soxhlet extractor. The resulting materials were characterized by XRD, N_2 adsorption isotherms, TG, XPS, SEM, TEM, UPS and Uv-Vis.

Results and discussion.

The synthesized materials are crystalline, their XRD pattern matchs with the characteristic peaks of the starting MOF (NH_2-MIL-125), suggesting that the crystallinity of the material does not change with exchange. The morphology of the crystals also remained unchanged to the initial one (disk-shaped crystals). The specific BET surface area of the materials decreased (700-1000 m^2/g aprox.) with respect to the starting MOF (1114m^2/g), however, the isotherms of all of them are characteristic of microporous materials (see Figure 1). All the materials show thermal stability up to 400˚C. The band gap of the materials was determined by UV-Vis diffuse reflactance, and it is evident that with the inclusion of M metals the value of this band has shifted to lower values, the band gap values are between 2.13eV and 2.41eV, which makes these materials can be used in photocatalysis under visible light.

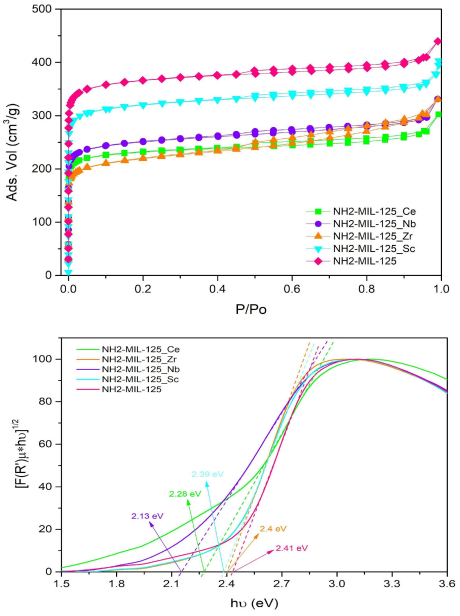

Figure 1. N_2 adsorption isotherms (up), Tauc Plots (down).

Acknowledgments

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Operando spectroscopic study of Cu-MOFs for direct methane to methanol conversion: a comparison of different Cu ligands

V.Finelli[1,2], E. Aunan[3], B. Centrella[1], G. Deplano[1], B. Garetto[1], N. G. Porcaro[1], M. Bonomo[1], A. Damin[1], M. Signorile[1], E. Borfecchia[1], B. G. Solemsli[3], S. Prodinger[3], C. Barolo[1], P. Szilagyi[3], K.P. Lillerud[3], U. Olsbye[3]*, S. Bordiga[1]*

[1]*Department of Chemistry, NIS and INSTM Reference Centre, University of Turin, Via P. Giuria 7 I-10125 and Via G. Quarello 15/A I-10135, Turin, Italy*

[2]*Istituto Universitario degli Studi Superiori (IUSS), Palazzo del Broletto, Piazza della Vittoria 15 I-27000, Pavia, Italy*

[3]*Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, Sem Sælands vei 26, N-0315 Oslo, Norway*

**silvia.bordiga@unito.it *unni.olsbye@kjemi.uio.no*

Keywords: Cu-MOFs, direct methane to methanol, operando spectroscopy

Introduction. The activation of C-H bonds is a key challenge in modern chemistry: indeed, considering partial oxidation reactions, the conversion of light hydrocarbons to the corresponding industrially valuable alcohols (e.g. direct methane to methanol, DMTM) would be a stepping stone towards a circular economy. Cu catalysts from biological origin, have proved their effectiveness in such processes but are fragile [1], while the synthetic analogues showed moderate activity and require reaction times beyond those applicable in an industrial context [2][3]. Cu-MOFs, featuring thermal and chemical stability intermediate of inorganic and organic systems, and containing a local Cu environment mimicking that of efficient enzymatic systems (e.g., LMPO) could overcome such limitations, potentially yielding a system with high turn-over frequency (TOF) and -number (TON) at mild temperatures.

Experimental/methodology. A set of potentially active Cu-MOF catalysts have been synthesized, thoroughly characterized and tested for DMTM. An isothermal (150 °C) stepwise protocol, adopting O_2 as the oxidant, was designed on the basis of previous literature.[3] Samples belonging to the UiO-6X family have been modified with bio-inspired anchoring sites for Cu ions. Beside basic characterization, each material has been investigated through operando spectroscopies (UV-vis and XAS), unveiling relevant details on the redox behavior of the Cu ions during the sequential reaction steps while quantitatively assessing the catalytic performances.

Results and discussion. Some of the considered materials (e.g., both Cu-UiO-66 featuring histidine as anchoring site and Cu-UiO-67 whose original linker has been partially replaced by methylated bipyridine) presented interesting features, exhibiting a quantitative redox cyclability among Cu(I)/Cu(II) by modifing the gaseous environment from inert to reducing/oxidizing. These materials also displayed excellent hydrothermal stability after the treatment, making them interesting candidate catalysts for the direct methane to methanol conversion at mild temperature.

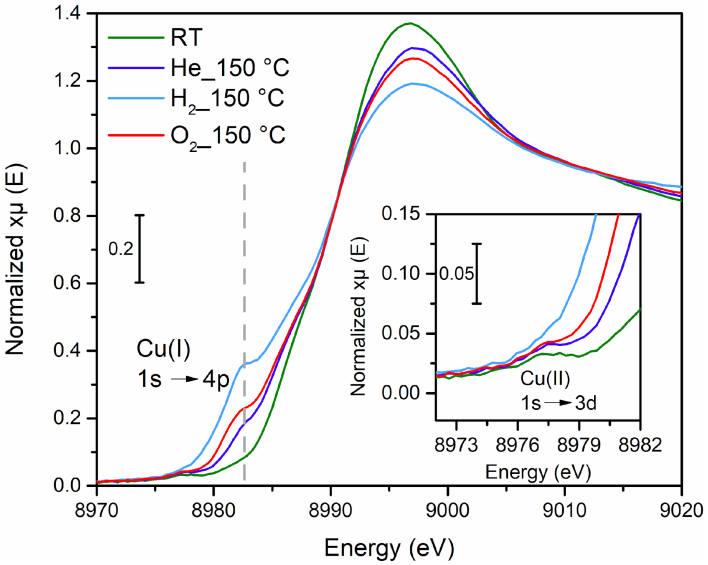

Figure SEQ Figure * ARABIC 1 – XAS evolution spectra of Cu-UiO-66-his upon different gas flows.

Acknowledgments

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Nb_2O_5-P_2O_5-SiO_2 catalysts: a focus on surface acidity.

E. Finocchio[1*], G. Garbarino[1], G. Busca[1], A. Gervasini[2], S. Campisi[2], B. Silvestri[3], C. Imparato[3], A. Aronne[3]

[1]*Dipartimento di Ingegneria Civile, Chimica e Ambientale, Università di Genova, Genova, Italy.*

[2]*Dipartimento di Chimica, Università degli Studi di Milano, Milano, Italy.*

[3]*Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, Napoli, Italy.*

[*]*Elisabetta.Finocchio@unige.it*

Keywords: FT-IR spectroscopy, Acidic Oxides, Niobia, Phosphoric Anhydride, Silica.

Introduction. The Nb_2O_5-P_2O_5-SiO_2 (Nb-P-Si) mixed oxide system is reported as an environmentally friendly and performant solid catalyst in the field of conversion of biomass-derived chemicals [1-3]. In fact, the ensemble of moderately strong protonic acid sites and Lewis acid sites results in an efficient activation of n-type bases such as oxygenates compounds. The tunable distribution of both Brønsted and Lewis acidic sites combined with high stability towards hydrolysis given by Nb–O–P bonds make this catalytic system of increasing importance in industrial chemistry. In this work we report results on the nature and the amount of exposed acidic sites, that have been investigated through complementary techniques, and on ethanol and diethylether conversion on niobium-phosphorus-silicon mixed oxides.

Experimental. Two samples were prepared with different Nb/P molar ratio, whose nominal composition are $2.5Nb_2O_5{\cdot}2.5P_2O_5{\cdot}95SiO_2$ and $5Nb_2O_5{\cdot}2.5P_2O_5{\cdot}92.5SiO_2$, according to the hydrolitic sol gel synthesis procedure previuosly described [4]. Acid site titration has been carried out in solid-liquid phase using 2-phenylethylamine (PEA) as probe and by ammonia adsorption and thermodesorption (TPD) experiments. FT-IR surface transmission experiments have been carried out over pure powder disks activated in vacuum and following adsorption of Pyridine, Ethanol and Diethylether. Spectra of the pure powder disks were recorded at each adsorption/desorption step, using a Thermonicolet Nexus instrument (100 scans, DTGS KBr detector). Experiments on ethanol conversion have been realized both in the Temperature Programmed Reaction mode and in steady state conditions (1 mol%, and 2.5 or 3 mol% of ethanol in pure N_2 or in O_2/N_2 mixture) in tubular fixed bed reactor using FT-IR spectrometer as detector.

Results and discussion. Amorphous Nb-P-Si catalysts have been obtained with a combination of mesoporosity and microporosity and retaining a surface area around 400-350 m^2/g after calcination. IR experiments show a quite heterogenous surface characterized by the presence of Si-OH, POH and/or NbOH groups. Therefore, the samples posses weakly acidity together with Brønsted acidity sufficiently strong to protonate pyridine and medium-strong Lewis acidity due to Nb^{5+} exposed ions. Both IR experiments and ammonia adsorption and thermodesorption experiments indicate that acidity increases at increasing Nb concentration. On the other side, the use of a bulky molecules such as PEA for adsorption experiments in liquid phase evidences the different accessibility of acid sites, lower in the sample having the lower Nb content due to smaller micropores. It is confirmed that the increased amount of niobia results in an increased concentration of surface acid sites. These materials are active in the gas-phase, acid-catalyzed, ethanol dehydrogenation to ethylene starting from around 500 K, while the formation of diethylether is minimal. Traces of acetaldehyde from ethanol dehydrogenation are also detected. The sample richer in niobium is indeed more active. In our conditions, some catalyst deactivation is found, which is more significant at low temperature. IR spectra confirm the data of catalytic experiments, showing the formation of adsorbed species, likely alkoxides, that decompose mostly to ethylene above 500 K [5]. The spectroscopic analysis of the spent catalyst shows that the surface is still hydroxylated, with a small increase in the Bronsted sites/Lewis sites ratio.

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Strong metal support interaction studied with operando electron microscopy

H. Frey,[1] A. Beck,[2] X. Huang,[3] J. A. van Bokhoven,[1,4*] M.-G. Willinger[5*]
[1]*ETH Zürich, Zürich, Switzerland*
[2]*UCSB, Santa Babara, USA*
[3]*Fuzhou University, Fuzhou, China*
[4] *PSI, Villigen, Switzerland*
[5] *TUM, Garching, Germany*
[*]*jeroen.vanbokhoven@ethz.ch, marc.willinger@tum.de*

Keywords: SMSI, operando electron microscopy, heterogeneous catalysis

Introduction.

Strong metal-support interaction (SMSI[1]), i.e. the reversible encapsulation of platinum group metals under reducing atmosphere and high temperature is known to modify the catalyst's adsorption properties, thereby altering its selectivity[2] and enhancing its resistance to sintering.[3] However, the details of how the overlayer interacts with the metal surface and the gas molecules during the catalytic cycle can only be studied operando since the system will undergo significant transformations when removed from the reaction chamber.(Environmental) TEM proved vital in this research[4] but despite significant discoveries, and partly due to resolution and pressure constraints,[5] the full picture of SMSI remained elusive.

Experimental/methodology.

We recently performed a series of operando TEM experiments in an attempt to expand the conceptual understanding of SMSI and its potential applications. Operando TEM, in contrast to environmental TEM allows to study the catalyst under high pressures, and therefore, insights into the catalyst structure under conditions typically used in catalysis studies is possible. As most of SMSI research traditionally focused on the catalyst's state under reducing atmospheres, little is known about the mechanism responsible for overlayer retraction, its state under reactive conditions or under oxidative conditions.

Results and discussion.

Our experiments revealed that the encapsulated state of platinum particles is maintained when the catalyst is exposed to oxygen at high temperature, in this case by an oxidized form of the SMSI layer.[6] Targeted encapsulation under oxygen prevents the evaporation and sintering of platinum when exposed to oxygen at high temperature.[7] The overlayer retracts in the co-presence of hydrogen and oxygen and, under reactive redox conditions, i.e. during the simultaneous presence of hydrogen and oxygen, the system adapts a dynamic behavior and thus reveals yet another manifestation of metal support interactions.[8]

The work shows that the state of the catalyst under reactive conditions differs significantly from the well-studied, classical SMSI state, highlighting the need for operando TEM studies for our understanding of the behavior of an active catalyst and thus, the structure activity correlation relevant for catalytic function. It also reveals how the exact sequence of treatments determines the stability of the nanoparticles induced by the presence respectively absence of titania overlayers. Reversible overlayer formation in oxygen has the potential to operate noble metal catalysts in harsh environments and to protect such catalysts from sintering during burn-off cycling.

Acknowledgments
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Lithium/copper/aluminum oxides based on LDH structures: redox and acidobasic properties

K. Frolich*, J. Malina, O. Chovanec, M. Hájek

Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic
**karel.frolich@upce.cz*

Keywords: LDH, mixed oxide, lithium, copper, aluminum, redox, acidobasicity

Introduction

Present contribution is dedicated to the preparation and characterization of layered double hydroxides (LDH) and derived mixed oxides comprising lithium (I) and aluminum (III) ions. The possibilities to introduce copper (II) ions during the LDH synthesis in order to produce precursors of Li-Cu-Al mixed oxides with tunable redox and acidobasic properties are studied. The aim is to highlight main specifics related to previously described copper (II) containing LDH/mixed oxides with Mg (II) ions and Al (III) ions (hydrotalcite-like materials). Prepared Li/Cu/Al LDH are considered as catalysts or catalysts precursors which can be exploited for example in the Guerbet reaction [1,2] for conversion of primary alcohols to higher alcohols, as it comprises de/hydrogenation steps (redox centers), aldol condensation step (basic centers) and dehydration step (acidic centers).

Experimental

The urea method [3] is introduced for preparation of the Li-Al type LDH precursors. A batch reactor with reflux condenser at atmospheric pressure was used for the co-precipitation. Respective amounts of lithium, aluminum (and copper) nitrates at specified molar ratios of metals were dissolved in redistilled water. Solution was transferred into a batch reactor, followed by heating near to the boiling point. The urea was added to adjust pH and start the co-precipitation of hydroxides. The LDH precursors were calcinated to obtain mixed metal oxides. The chemical composition of prepared LDH was studied by the ICP-OES. The phase purity and LDH to oxide transformation was studied by the X-ray diffraction. The textural properties were derived by the N_2-physisorption. The redox properties related to copper were studied by the H_2-TPR method. The acidobasic properties were studied by the CO_2- and NH_3-TPD methods.

Results and discussion

Sharp XRD diffraction lines related to the LDH structure verified succesfull synthesis of Li-Al LDH by the co-precipitation with urea. Well crystalline LDH products were obtained. LDH precursors precipitated with Li/Al molar ratio of 1/2 (maximum), a stoichiometric excess of lithium in the solution was needed. The addition of copper during the co-precipitation with urea led to production of ternary Li-Cu-Al LDH, but the amount of introduced copper was limited. The LDH precursors were transformed to mixed metal oxides, which properties were related to the metal ratio in the parent co-precipitation solution. Standard H_2 reduction profiles with repeated oxidation/reduction cycles suggested the interaction of copper with the Li-Al support. The desorption experiments showed that the total concentration of Lewis basic sites and population (density) of strong basic sites (O^{2-}) was higher to often studied LDH derived Mg-Al mixed oxides. LDH based Cu-Li-Al mixed oxides represent relatively cheap tunable bi-functional catalyst.

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The distribution and relocation of copper species in Cu-molecular sieves with different topologies: an EPR investigation

Q. Gao[1], S. Mossin[2*]

[1,2] *Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, Kemitorvet 207, 2800 Kgs. Lyngby, Denmark.*
[*] *slmo@kemi.dtu.dk*

Keywords: Cu-based catalysts, EPR, copper distribution, copper relocation, redox properties

Introduction

Copper exchanged zeolites or molecular sieve are attractive because they facilitate various oxidation reactions and redox cycles.[1] This includes selective catalytic reduction of NOx using ammonia (NH_3-SCR), NO decomposition and selective oxidation of methane to methanol. Copper is present as several different species depending upon the local zeolite structure and has high mobility at reaction conditions which challenges the characterization and detailed knowledge about these catalytic reactions.[2],[3] In this work, we will try to investigate the distribution and mobility of copper species in Cu-molecular sieve catalysts with different topology (CHA, AEI, MOR). We are also aiming to investigate effects on copper distribution in Cu-MOR synthesized by solvent-free methods.

Experimental/methodology.

Copper molecular sieves are synthesized using aqueous ion exchange at different copper concentrations. Both commercial and synthesized zeolites have been investigated.

Powder X-Ray diffraction (XRD) patterns, Scan electron microscopy (SEM), Solid-state NMR, and X-ray fluorescence spectroscopy (XRF) were employed to investigate the physical and chemical properties of the catalysts. In-situ and ex-situ EPR experiments were conducted to investigate the distribution and speciation of copper species in these catalysts.

Results and discussion.

Figure 1. Cu distribution in different Cu-molecular sieves determined by ex-situ and in-situ EPR.

The amount of redox-active Cu species differs significantly between the samples, although they have a similar amount of EPR active Cu in the fresh samples. Cu-CHA possessed the highest amount of redox-active Cu. The redox-active Cu in Cu-CHA-10 and Cu-AEI-50 can be assigned to one type of copper site (Site B in Fig. 1). Xue et al.[4] concluded that Site B in Cu-SAPO-34 is the main active site in low temperature (100-200°C) SCR reaction. We propose that the small amount of Site B in Cu-AEI-50 is the reason for the observed poor redox performance at 150°C.

The series of samples with the MOR topology have comparable amounts of Site A and B. The amount of redox active copper is not influenced by the synthesis method.

Acknowledgments

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Influence of Precursors Structure on Active Phase Formation of Co-Mo Ammonia Synthesis Catalysts

P. Adamski[1,2*], D. Moszyński[2]

[1]*Faculty of Natural Sciences, Institute of Chemistry, Materials for Innovative Energy Concepts, Technische Universität Chemnitz, 09107 Chemnitz, Germany*
[2]*Department of Chemical and Environment Engineering, West Pomeranian University of Technology in Szczecin, 71-065 Szczecin, Poland*
[*]*pawel.adamski@chemie.tu-chemnitz.de*

Keywords: ammonia synthesis, cobalt molybdenum nitrides, ammonolysis

Introduction. The calculated volcano-shaped relationship between ammonia synthesis activity and nitrogen adsorption energy [1] indicates that the active sites consisting of cobalt and molybdenum atoms are located near the top of that curve. The high catalytic activity of Co-Mo nanoparticles supported on CeO_2 [2] and the bulk cobalt molybdenum nitrides Co_2Mo_3N, Co_3Mo_3N [3,4] was experimentally proven. The method for the synthesis of cobalt molybdenum nitrides consists of the preparation of the oxidic precursor and the subsequent ammonolysis [5]. The parameters of the precipitation process affect the composition of the precursor, and properties of the catalysts. Despite the large number of works regarding cobalt molybdenum bimetallic oxides, there are very few reports about their transformation to the nitride state. Thus, this work focuses on the influence of the precursor structure on the active phase formation and catalytic properties of cobalt molybdenum nitrides.

Experimental. Oxidic precursors were obtained by precipitation from water solutions of cobalt(II) nitrate and ammonium heptamolybdate at different pH values controlled by the addition of aqueous ammonia. The ammonolysis of the precursors was investigated with the use of the reaction chamber attached to a diffractometer. This approach allowed *in-situ* X-ray powder diffraction studies of the ammonolysis process. The activity of catalyst in ammonia synthesis was measured with the use of a plug-flow laboratory reactor.

Results and discussion. The precursors obtained from acidic solutions consist of $CoMoO_4 \cdot 0.9H_2O$ phase, whereas those precipitated from basic solutions consist of $NH_4Co_2OH(MoO_4)_2 \cdot H_2O$ phase. The water removal from the $CoMoO_4 \cdot 0.9H_2O$ phase or water and ammonia removal from the $NH_4Co_2OH(MoO_4)_2 \cdot H_2O$ phase takes place during calcination, in the both cases resulting in formation of the cobalt molybdate $CoMoO_4$ phase. The further decomposition of the $CoMoO_4$ proceeds yielding the bimetallic oxide $Co_2Mo_3O_8$ and the cobalt(II) oxide CoO. Exposure of both oxides to the ammonia atmosphere results in the formation of the intermetallic compound Co_3Mo and metallic cobalt as intermediates. During further nitriding these phases form cobalt molybdenum nitrides Co_3Mo_3N and Co_2Mo_3N. The catalyst obtained from the precursor precipitated at pH 5.5 was composed of Co_3Mo_3N and Co_2Mo_3N nitrides, and the catalyst obtained from the precursor precipitated at pH 7.5 additionally contained the Co_3Mo intermetallic compound. The catalyst obtained from the precursor precipitated at pH 7.5 was the most active. The presence of the Co_3Mo intermetallic phase in the catalyst was shown to have a positive effect on the activity of these materials in the ammonia synthesis process. Both catalysts are more active in the ammonia synthesis reaction than the industrial iron catalyst.

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Activity and stability of catalysts deNOx/deN2O Nitric Acid Process

A. Garbujo[1*], F. Oldani[1], R. Lanza[2], A. Lahougue[3], E. Rohart[3], P. Biasi[1].

[1]*Casale SA, Lugano, Switzerland*
[2]*Verdant, Stockholm, Sweden*
[3]*Alsys, Ploemeur, France*
[*]*Corresponding Author's E-mail address: a.garbujo@casale.ch*

Introduction

Nitrous oxide (N2O) is one of the most impacting greenhouse gasses that significantly contributes to climate change. In 2017, Europe alone emitted around 18 million tonnes of N2O, mainly from agricultural activities and the production of nitric acid. [1] Scientist are constantly searching for effective new deN2O catalysts that can be used in real-world applications. One crucial aspect of this research is the industrial aging of catalysts. This process simulates the conditions under which catalysts will be exposed to in industrial environments, including high temperatures and exposure to pollutants. By conducting representative industrial aging tests, researchers can gain a better understanding of how catalysts will perform over time in real-world settings and make necessary adjustments to improve performance and lifetime. Additionally, this process allows researchers to identify potential degradation mechanisms and optimize catalyst design, thus reducing N2O emissions in the final stages of catalyst use. In this study, the performance of Fe-FER and Fe-ZSM5 catalysts were evaluated through simulated industrial aging tests.

Experimental/methodology

Industrial Fe-FER and Fe-ZSM5 catalysts were prepared by the French company ALSYS on an industrial scale. [2] The catalysts were exposed to a simulated accelerated aging procedure, which was created to model a specific catalytic aging process. This was done to study the deNOx/deN2O catalytic behavior at the end of the catalyst's life. The deNOx/deN2O catalytic performance was tested under relevant industrial conditions in an Inconel reactor. The conditions for deN2O reaction were as follows: NO 70 ppm, NO_2 30 ppm, N_2O 900 ppm, O_2 3.0%, H_2O 0.3% and N_2 balance. The conditions for deNOx were as follows: NO 325 ppm, NO_2 325 ppm, N_2O 40 ppm, NH_3 650 ppm, O_2 3.0%, H_2O 0.3% and N_2 balance. A very high space velocity was used to stress the differences in catalytic activity between the catalysts that were tested. The aging treatments were conducted for 150 hours at two temperatures, 600 and 700°C. The detector used was FT-IR coupled with a lambda probe for oxygen measurement.

Results and discussion

This study compares the catalytic activity of Fe-FER and Fe-ZSM5 catalysts for NO_x and N_2O abatement in a simulated nitric acid process. The study examines the structural, through XRD, and catalytic evolution of the catalysts upon aging under representative industrial conditions. The results show that Fe-FER has higher catalytic activity and structure stability than Fe-ZSM5, particularly after the aging procedure. Fe-ZSM-5 experiences loss in deN2O activity, while Fe-FER retains its catalytic activity under these conditions. The stability of the Fe-FER catalyst is believed to be responsible for its higher catalytic activity and better preservation of deN2O activity. The study also highlights the importance of using representative industrial aging treatments and real industrial test conditions when studying new catalysts, as these conditions can greatly affect the catalytic activity and structure of the materials. Further research is needed to fully understand the mechanism of the catalytic activity of Fe-FER and Fe-ZSM5 under real industrial conditions.

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The Power of Operando Lab-based X-ray Absorption Spectroscopy: Unravelling Synergistic Effects in Bimetallic CO_2 Hydrogenation Catalysts

N.S. Genz[1], A.-J. Kallio[2], F. Krumeich[3], S. Huotari[2], F. Meirer[1], B.M. Weckhuysen[1*]
[1]*Utrecht University, Inorganic Chemistry and Catalysis, Utrecht, The Netherlands*
[2]*University of Helsinki, Department of Physics, Helsinki, Finland*
[3]*ETH Zürich, Laboratory of Inorganic Chemistry, Zürich, Switzerland*
[*]*b.m.weckhuysen@uu.nl*

Keywords: Lab-X-ray Absorption Spectroscopy, Operando Characterization, Multi-Metal Catalysts

Introduction. Thermocatalytic conversion of CO_2 towards value-added products constitutes a promising starting point to mitigate continuously increasing global CO_2 emissions and associated climate change. Ideally, the captured CO_2 is converted with only sustainably produced hydrogen into value-added products. However, for achieving this goal, the search for the optimal catalyst constitutes a major challenge. For the rational design of next generation catalyst formulations, appropriate characterization tools and performing *operando* experiments are indispensable for deducing a fundamental understanding of structure-performance correlations of catalysts.[1] In this context, the new possibility to perform *operando* lab-based X-ray absorption near-edge structure (XANES) analysis quasi-simultaneously at multiple absorption edges paves the way for a new era of catalyst characterization.[2] Here, we showcase the power of *operando* lab-XANES by unravelling insights into synergistic effects of bimetallic CO_2 hydrogenation catalysts.

Experimental/methodology. The catalysts comprise Ni-Fe and Ni-Cu bimetallics supported on a SiO_2 support with a total metal loading of 6 wt%. The self-designed *operando* lab-based XANES setup is based on a Johann geometry, where the spherically bent crystal analyzers are located in a crystal exchanger and the catalyst is deposited in a motorized sample cell stage being connected to a gas chromatograph.

Results and discussion. Based on detailed *operando* studies, we unraveled a correlation between decreasing Ni/Fe ratio and decreasing particle size, increasing reoxidation of the Ni and Fe species during CO_2 hydrogenation, and a shift of the product selectivity towards CO together with the production of C-C coupling products. Interestingly, the reducibility was found to be Ni/Fe ratio-independent except for a ratio of 2. Moreover, exchanging Fe by Cu induced a facilitated reducibility of the Ni species and a more stable selectivity during CO_2 hydrogenation with CO being the main reaction product, while the reoxidation behavior remained unaffected. The presented results from catalyst screenings with *operando* lab-XANES showcase the power of such studies and their importance for justifying and planning topically focused synchrotron-based studies, which, in combination with lab-based studies, are essential in taking steps towards a more rational design of improved catalysts and our journey towards a more circular society.

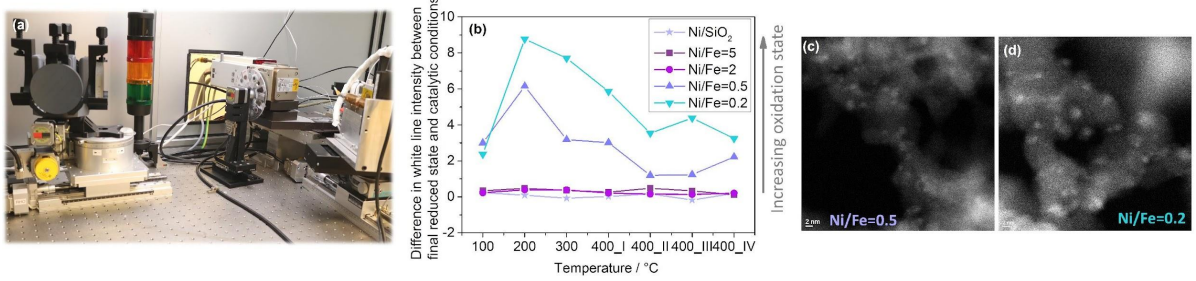

Fig.: *Operando* lab-based X-ray absorption near edge spectroscopy (XANES) setup (a), difference in the white line intensity of the Ni K-edge XANES under CO_2 hydrogenation conditions (H_2/CO_2=4, 1 bar, b), and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images for two different Ni/Fe ratios (c, d).

Acknowledgments
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Unraveling the Catalytic Role of Pt SingleAtom Catalysts in Acetylene Hydrochlorination by Operando Xray Absorption Spectroscopy

V. Giulimondi[1*], G. Giannakakis[1], I. Surin[1], A.H. Clark[2], J. PérezRamírez[1]

[1]*ETH Zürich, Zürich, Switzerland*
[2]*Paul Scherrer Institute, Villigen, Switzerland*
[*]*vgiulimondi@ethz.ch*

Keywords: singleatom catalysis, operando X-ray absorption spectroscopy, acetylene hydrochlorination.

Introduction. Vinyl chloride (VCM) manufacture via acetylene hydrochlorination is a longestablished industrial process that runs over toxic mercurybased catalysts,[1] demanding sustainable alternatives. Carbonsupported Pt singleatom catalysts (SACs) have emerged as compelling candidates owing to their high activity and unparalleled stable performance.[2] Still, their catalytic behavior is largely dependent on the metal speciation and properties of the carbon host,[2] calling for mechanistic studies to identify structureperformance relations and ultimately unlock the potential of carbonsupported metal SACs.

Methodology. Herein, we investigate the synthesis and catalytic function of Pt single atoms with varying Cl^- ligand coordination on different carbons via operando Xray absorption spectroscopy.

Results and discussion. We unveil the role of Pt sites as the mediators of chlorine supply to the carbon matrix, which adsorbs C_2H_2 and catalyzes VCM evolution (**Fig. 1**). The chlorination activity is found to depend on the metal atom coordination environment, dictated by the synthetic strategy as well as the carbon host composition and properties. These insights, corroborated by the analysis of other noblemetal SACs, pinpoint the role of both the metal sites and the carbon host to develop acetylene hydrochlorination sustainable catalysts.

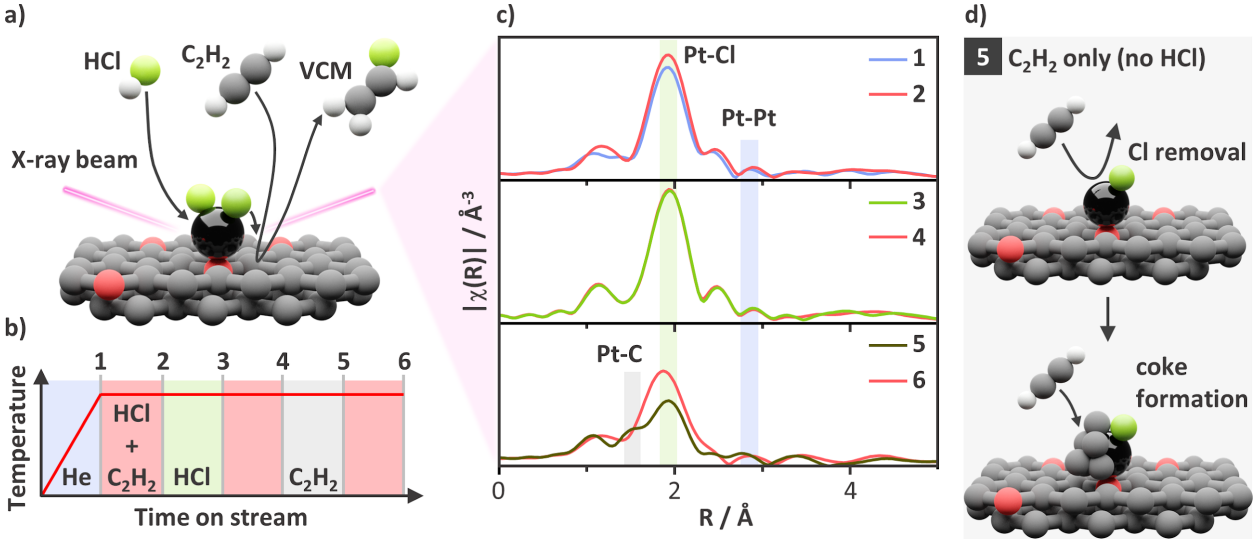

Figure 1. (a) Schematic representation of the catalytic function of Pt single atoms derived via timeresolved XAS analysis (b) under varying reactive atmospheres, together with (c) the corresponding Pt L_3 EXAFS spectra. (d) Representation of the impact of a C_2H_2 atmosphere on the metal sites. In the absence of HCl, C_2H_2 progressively dechlorinates the metal site and binds onto it, eventually forming coke.

Acknowledgments
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Methane oxidation to methanol by operando UV-vis-IR spectroscopy. The role of type, location and number of Fe sites in mordenite.

K.A. Tarach[1], J. Sobalska[1], A. Held[2], K. Góra-Marek[1]

[1] *Faculty of Chemistry, Jagiellonian University, Kraków, Poland*
[2] *Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland*

Introduction. Extra-framework Fe species are considered as the active site for the formation of an α-oxygen species which are formed by decomposition N_2O over the α-Fe^{2+} site. After oxygen addition mononuclear $Fe^{4+}=O^{2-}$ (or Fe^{3+}-$O^{\bullet-}$) or dinuclear oxo-bridged $Fe^{3+}O^{2-}Fe^{3+}$ species were proposed as the most appropriate models for the α-oxygen active site. Very recently, oxygen molecule activation over Fe-ferrierites was achieved by two cooperating distant Fe cations [1, 2]. This binuclear cationic Fe(II) centers are close enough to cooperate in splitting O_2 at RT resulting in the a pair of α-oxygen species. This reveal facile oxidation of Fe(II) cations can be explained by the unique topology of the ferrierite zeolite offering a proper Al atoms arganization in 8-MR channels, namely two negatively charged Al atoms in Al–O–Si–O–Si–O–Al sequence. In mordenite, the conditions required for balancing a bare divalent cation are met for the cations in 8-ring channels rather than in 12-ring channel. Therfore we investigated the catalytic performance of Fe-mordenites of various Fe loading and Al content assuming that this two papameters influence most the speciation of iron sites.

Methodology. The methane oxidation over Fe-MOR catalysts (Si/Al=8.4 and 14.6) of various Fe-loading (0.1, 0.5, 1.0 % wt.) and H-counterparts was monitored by *operando* DR-UV-vis-GC-MS and *operando* Vis-NIR-MIR-CG-MS to get the insigth into the nature of adsorbed species (IR) and recognize the coordination sphere and the evaluation of the metal–ligand interaction strength during the reaction (UV-Vis-NIR). Finally, the correlation between catalytic activity and selectivity was established.

Results and discussion. Our results indicate that at the lowest Fe content, the redox species are located in 8-ring channels forming either isolated Fe^{2+}or Fe^{III}-OH sites as major species in zeolites of lower and higher Al content in framwork, respectively. Methane oxidation to methanol identified by its IR and UV-vis spectroscopic features has to be assigned exclusively to α-O sites originating from Fe^{2+} ions located in 8-ring channels. The mononuclear $Fe^{4+}=O^{2-}$ formed in the reaction of Fe^{2+} with O_2 are more reactive than Fe^{III}-OH or binuclear Fe^{III}-(O)-Fe^{III} in selective oxidation of methanol. The oxidation ability of the latter has however negative impact on methanol selectivity at higher temperatures.

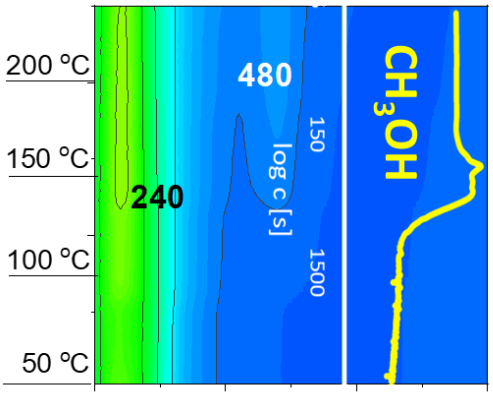

Fig. 1. *Operando DR UV-vis spectra and MeOH mass signal evolution for methane oxidation at various temperatures.*

Acknowledgments

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Tracking Transformation of Reagents in Zeolites: 2D COS Rapid Scan IR and UV-vis Spectroscopic Approach

K.A. Tarach[1], W.Chen[2], E.A. Palomares[3], J. Martinez-Triguero[3], A. Zheng[2], K. Góra-Marek[1]*

[1] *Faculty of Chemistry, Jagiellonian University in Kraków, Poland*
[2]*State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, APM, CAS, China*
[3]*Instituto de Tecnologia Quimica (UPV – CSIC), Valencia, Spain*
kinga.gora-marek@uj.edu.pl

Introduction. Metodology. Time-resolved IR spectroscopic studies conducted over a temporal range counted from seconds to several dozen milliseconds provide the possibility to detect short-living intermediate reactive species and their mutual relationships crucial for a thorough understanding of the reaction pathways. Rapid scan spectroscopy (IR, UV-Vis) enables to track the phenomena inherent to each catalytic process, i.e. diffusion, adsorption, and surface reaction, all of them in the appropriate time domain and under conditions required for the working catalyst (*operando*). Operando aproach successfully combines all the UV-Vis and IR spectoscopic characteristics with catalyst activity and selectivity and allows to describe reaction pathway under realistic conditions. Working in *operando* rapid scan regime (high temperature, flow conditions) results in collecting the very extensive spectrum data of extremely both low intensity and complexity of the bands. Implementation of two-dimensional correlation analysis to spectroscopic data (2D COS RS UV-Vis-IR spectroscopy) attained for catalytic processes affords identification of spectral features of intermediate species confined inside the micropores of zeolites and the sequence of the appearance of the intermediate on the catalyst surface.

Results and discussion. Transformation of zeolite-confined small hydrocarbons and hydrocarbons derivatives was investigated to define nanoscale effects, reaction path, thus catalytic properties. Several cases, most representative of the 2D COS IR and UV-vis methodology, are cited.

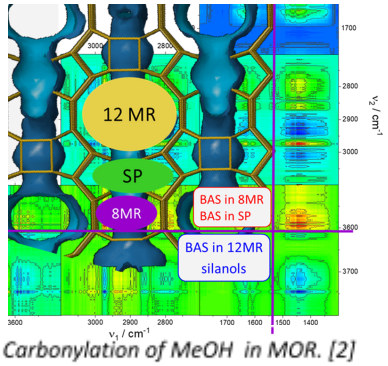

Fig. 2. *Carbonylation of MeOH in MOR. [2]*

The roles of ketene and its derivates (i.e. acylium ion and surface acetyl) associated with direct C-C bond coupling during carbonylation reaction investigated thoroughly by 2D COS rapid scan IR spectroscopy [1, 2]. Unique acylium ion was observed exclusively in H-MOR confirming the specificity of the 8-MR pores activity. In contrast, the surface acetyl species were identified in H-SSZ-13 as the predominant species. The FT-IR time-resolved *operando* study revealed also that the reaction pathway in ethanol transformation over ZSM-5 is controlled by the proximity of aluminium atoms in the framework. The zeolite ZSM-5 containing mostly isolated Al atoms was found to transform ethanol in the associative pathway, while over ZSM-5 containing a dominating fraction of two aluminium atoms in one ring the ethanol molecules were converted in the dissociative route. The combined 2D COS UV-vis and 2D COS rapid scan IR methodologies were beneficial in resolving the EtOH oxidation path by defining the status of manganese phase and the speciation of surface intermediate species. Finally, the mechanisms of EtOH oxidation governed by the basicity of ZSM-5 were discriminated. All these findings indicate that the 2D COS spectroscopy is a versatile tool particularly addressed to understanding the transformation of small molecules confined in zeolites.

Acknowledgments
The work was supported by the National Science Centre, Poland, under Grant No. 2021/41/B/ST4/00048.

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Surface science behind CuO catalytic efficiency

S. Górecka* and K. Pacultová

Institute of Environmental Technology, CEET, VSB-Technical University of Ostrava, 17. listopadu 15/2172, 708 00 Czech Republic
sylwia.gorecka@vsb.cz

Keywords: copper oxides, cerium oxides, cerium-copper, ammonia oxidation

Introduction. Ammonia, NH_3, is one of the air pollutants thats' release is strictly monitored due to its high impact onto both, human's health and environment. Modern catalysis gives the opportunity to reduce the ammonia release by the application of the selective catalytic oxidation process (NH_3-SCO). This topic was the main theme of our previous research [1-3]. We studied the relation between physico-chemical properties of copper oxide species and its efficiency as catalysts of NH_3-SCO. We put the special effort to study aspects like copper accessibility on surface, its dispersion, reducibility or interaction with the Ce as surface dopant.

Experimental/methodology. Our work focused on the Cu-containing mixed metal oxides obtained by calcination of hydrotalcite-like materials at temperature 800 °C. The goal was to obtain the thermally stable material of complex phase composition, that will not show any effects of structure re-organisation (*memory effect*). At second step of study, we incorporated cerium onto the materials surface to study synergistic redox relation between the Cu and Ce.

Materials characterisation was performed with use of several techniques: XRD, H_2-TPR, O_2-TPO, NH_3-TPD, reactive frontal chromatography, SEM(EDS) or XPS. The catalytic test was performed in self-build quartz-flow reactor system with the online FTIR detection.

Results and discussion. Our materials were complex mixture of simple oxides (MgO, CuO) and the spinel structure of general stoichiometry close to $M^{2+}Al_2O_4$. We have found that the copper loading approx. 10 - 15 mol. % allowed total ammonia conversion up to 350 °C. However, the high catalysis activity was not accompanied by satisfactory N_2 selectivity. On the other hand, materials with lower Cu loading (5 - 7 mol. %) showed better N_2 selectivity, but lower catalytic activity. Comparison of catalytic tests results with the materials characterisation allowed us to connect the formation of bulk-like and dispersed forms of CuO with the catalysts activity and selectivity, respectively.

At the same time addition of cerium was found to improve both N_2 selectivity and activity, regardless the copper mol. % loading. The XPS technique reveals occurrence of monovalent/divalent forms of Cu and trivalent/tetravalent forms of Ce. It allows us to consider possible Cu-Ce redox interactions. Occurrence of copper-cerium pairs results in formation of oxygen vacancies, thus improvement of O_2 storage capacity. Present of vacancies changed the reaction pathway, leading to rapid changes of Cu and Ce oxidation states: $Cu^{+} \leftrightarrow Cu^{2+}$ and $Ce^{3+} \leftrightarrow Ce^{4+}$, followed by release/refill of O_2. Oxygen reacts with adsorbed ammonia leading to the improvement of N_2 selectivity.

Acknowledgments
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Cobalt-containing high-silica ZSM-5 catalysts as efficient catalysts for ethanol steam reforming process: Operando UV-Vis and FT-IR spectroscopy investigation

G. Grzybek[1]*, M. Greluk[2], P. Stelmachowski[1], K. Tarach[1], G. Słowik[1], M. Rotko[1], K. Góra-Marek[1]

[1]*Faculty of Chemistry, Gronostajowa 2, 30-387 Krakow, Jagiellonian University, Poland*
[2]*Faculty of Chemistry, Maria Curie-Sklodowska University in Lublin, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland*
[*]*Corresponding Author: g.grzybek@uj.edu.pl*

Keywords: cobalt catalyst, ZSM-5 zeolite, silicalite, ethanol steam reforming, hydrogen production.

Introduction. In the face of climate change and the projected depletion of fossil fuel reserves, scientists are looking for alternative energy carriers. In this context, hydrogen is an important raw material, which production is becoming essential. It can be produced from bioethanol in the catalytic steam reforming process (ESR) using a wide range of catalytic systems including those based on the cobalt phase was investigated. The cobalt phase is usually spread over an oxide support e.g. Al_2O_3, CeO_2, or SiO_2 [1]. Zeolites with high porosity and a large specific surface area seem to be interesting to be applied as supports for the ESR cobalt catalysts. Relatively low interest in these materials results from their high selectivity towards the undesired C_2H_4 caused by their high acidity [2]. Fortunately, the path of ethanol dehydration to ethene can be significantly reduced or even eliminated by a controlled modification of the zeolite properties. The acidity of a zeolite catalytic system can be successfully adjusted either by doping with alkali or by decreasing the aluminum content in the structure.

Experimental/methodology. We synthesized a series of catalysts based on zeolite ZSM-5 with increasing Si/Al ratios (32, 750, Al-free zeolite) and different morphology (nanometric zeolite and micrometric) and tested their performance in the ethanol steam reforming process (500˚C, EtOH:H_2O 1:12, 21 h). We have checked the effect of potassium introduction on the Co|ZSM-5 catalyst. The samples were characterized with a wide range of methods (e.g. XRD, *in situ* XPS, SEM, TEM/EDX, H_2-TPR, RS, TG/DSC) and studied with the unique *operando* UV-Vis and FT-IR spectroscopy technique under the ESR conditions.

Results and discussion. The results pointed out a key role of the zeolite support acidity and morphology and indicated that their adjustment allows us to get the ESR catalyst with extraordinary catalytic parameters. The best catalyst, based on Al-free nanometric zeolite indicated 100% conversion of ethanol with >90% selectivity to H_2, elimination of C_2H_4 production, and >160 h stability in reaction conditions. Such great performance of the catalyst corresponds to a relatively low degree of carbon deposit formation, confirmed by the extensive *post-mortem* characterization and in-depth insight into the reaction mechanism with *operando* spectroscopic ESR studies. We attributed the strong advantage of nanometric zeolite support to the highest reducibility and dispersion of the cobalt phase. We also obtained promising results for the potassium-exchanged high-silica (Si/Al = 750) catalyst, still, the sample cannot compete with the one based on pure silica zeolite. The results of this study overthrow the existing paradigm of low activity and stability of zeolite-based ESR catalysts, opening the way to the development of competitive catalysts with a high application potential. To this end, new synthesis protocols should be optimized to obtain pure silica versions of zeolite materials.

Acknowledgments

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On the Role of Nickel in Doped MoO_3 Based HDO Catalysts

S. Haida[1], S. Löbner[1], H. Lund[1], A. Abdel-Mageed[1], S. Wohlrab[1], N. Escalona[2], C. Kubis[1], A. Brückner[1]

[1]*Leibniz-Institute for Catalysis, Rostock, Germany*
[2]*Pontificia Universidad Católica de Chile, Santiago de Chile, Chile*
[*]*christoph.kubis@catalysis.de*

Introduction

The hydrodeoxygenation (HDO) is a crucial step for valorization of lignocellulosic biomass derived pyrolysis oils. It is commonly conducted in the liquid-phase at high pressures (up to 150 bar) and moderate temperatures (100-250 °C). As the fast pyrolysis of lignin is done at T ≈ 500 °C and p ≈ 1 atm, these HDO conditions cause ineffective energy consumption and make it difficult to compete with cheap crude oil products.[1] Carry out the HDO process in gas-phase, would be an energy-efficient approach with regard to the entire process. This reaction can be done at 300 – 400 °C at normal pressure, near the pyrolysis conditions. Besides noble metal catalysts, MoO_3 is discussed as a catalyst that has a good activity and high arene selectivity.[2] In this study, we investigated Ni-doped MoO_3 catalysts, which tend to form a metal molybdate phase. Their catalytic behavior was tested, and investigations to understand the formation of active phases were performed.

Experimental/methodology

Phase pure MoO_3 and $NiMoO_4$ catalysts were used, as well as Ni/MoO_3 catalysts, where Ni is embedded as $NiMoO_4$. The Nickel loadings were 1 wt.% and 5 wt.%. Catalytic tests were conducted in a fixed-bed flow reactor for the gas phase HDO with anisole as a model substrate at 325 °C and p = 1 atm. Additionally, liquid-phase experiments were performed for comparison. In-situ XRD experiments were carried out to elucidate the active phase with a hydrogen/hydrocarbon treatment. Experiments using DRIFTS, TG-MS and XPS were conducted for supplementation.

Results and discussion

In most catalysts, a $MoO_xC_yH_z$ phase was observed after the reaction. This phase seems to have an influence on the catalytic activity, in agreement with reported results.[3] In the case of catalysts containing a small amount of nickel, the content of the $MoO_xC_yH_z$ phase was significantly increased (Fig 1.). It was also observed that phase pure $NiMoO_4$ is highly active, but shows a comparatively high methane selectivity. In these catalysts, the $MoO_xC_yH_z$ phase was not detected after the reaction nor during in-situ XRD experiments. The nickel is assumed to be the most active phase for hydrogen activation in this system. The obtained results will be compared to catalytic performance with other substrates (e.g., benzene) to gain further insights into the behavior of different active phases and the different factors for optimizations.

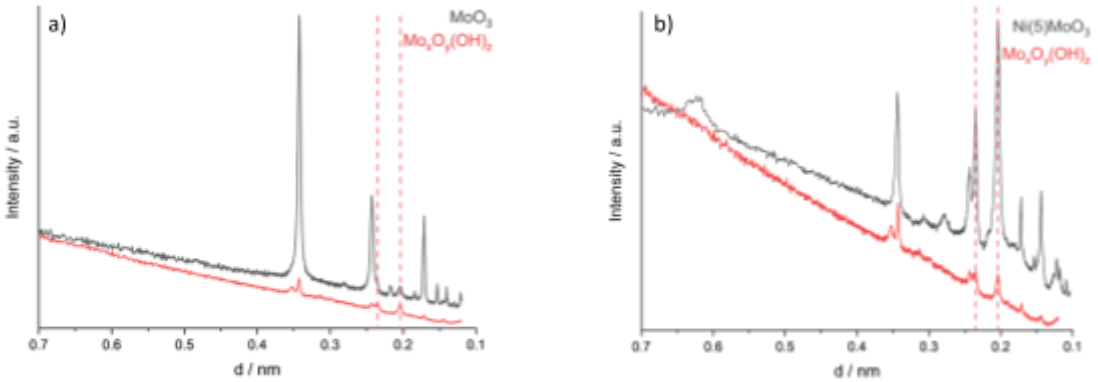

Figure SEQ Figure * ARABIC 1:a) Formation of $MoO_xC_yH_z$ in MoO_3 b) Formation of MoOxCyHz in Ni(5)MoO_3 compared to the result starting from molybdenum blue ($Mo_xO_y(OH)_z$) Both treated at 325 °C in H_2/CH_4 (1:1); — $MoO_xC_yH_z$ phase

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Characterization of NiMo catalysts with noble metal promoters

Filip Hallböök[1] , Tove Kristiansen[1,2] ,Jonas Elmroth Nordlander[1], Sabrina Gericke[3], Christian Hulteberg[1,2], Sara Blomberg[1]

[1]Department of Chemical Engineering, Lund University, 221 00 Lund, Sweden
[2]Hulteberg Chemistry & Engineering AB, 212 25 Malmö, Sweden
[3]Division of Combustion Physics, Lunds University, P.O. Box 118, 221 00 Lund, Sweden
** Correspondence: fi3077ha-s@student.lu.se*

Introduction.

To be able to face the challenges brought on by climate change, there is an urgent need to reduce the heavy dependence on fossil fuels. Bio-oil is one such renewable and carbon-neutral replacement that has shown promising potential. A key step in making bio-oil commercially feasible is the improvement of the catalytic hydrodeoxygenation (HDO) process. [1] One method to further develop the process is to improve the catalyst performance by the addition of promoters. Nickel and cobalt have commonly been used as promoters for Mo-catalysts [2], but there is potential for further improvement of the catalysts if other promoters can be found. This study aims to investigate the effects of adding four different noble metals to Ni-Mo oxide catalysts supported on δ-Al_2O_3 using two different synthesis methods.

Experimental/methodology.

The noble metal-NiMo/δ-Al_2O_3 catalysts were synthesized using incipient wetness impregnation. Two methods of including the noble metals in the catalyst synthesis were investigated, where the stage at which the noble metal was included in the synthesis was varied. To investigate the effect of the added noble metal, the reductive characteristics of the catalysts were studied using Quantitative Temperature Programmed Reduction (TPR). Furthermore, compositional analysis was performed using SEM-EDX.

Results and discussion.

Through the use of TPR we were able to identify a clear influence of the noble metal on the reduction behavior of the surrounding Ni-Mo oxide. The TPR curves for NiMo and Ir-NiMo catalysts are shown in Fig 1.

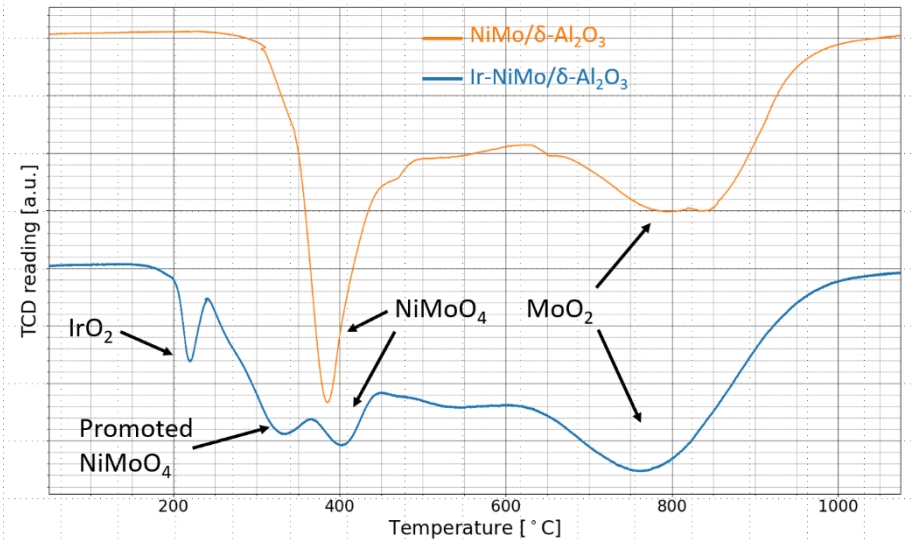

Fig. SEQ Fig. * ARABIC 1 Reduction characteristic of the studied catalysts.

Through the use of quantitative TPR the first peak of the Ir-NiMo curve could be identified as IrO_2. Further, a lowering of the reduction temperature of part of the Ni-Mo oxide could be observed when iridium was added to the catalyst. Being able to determine the influence of the noble metal even though a loading of 0.5wt% was used shows the power of TPR as an analytical method for the characterization of catalysts.

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The search for a new Deacon catalyst: modeling catalyst stability across the periodic table

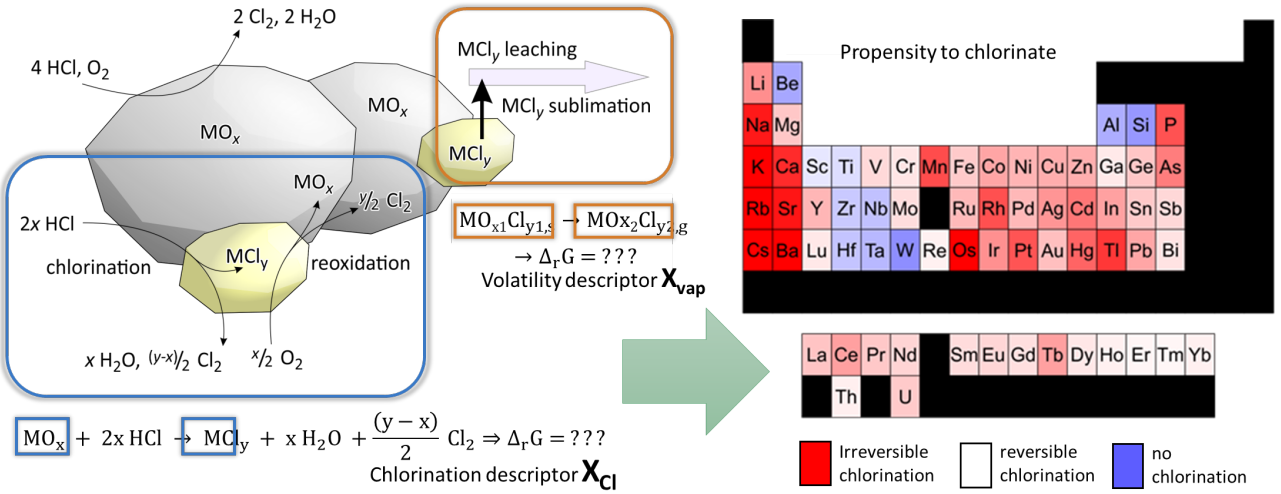
F. Hess[1,*]

[*]*Institute of Chemistry, Technical University Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany*

Keywords: catalyst degradation, modeling, screening, materials stability, Deacon process

Introduction. Catalysts degrade over time, which means that they lose catalytic activity or selectivity due to a variety of aging processes. While catalyst screening (both experimental and theoretical) regarding activity and selectivity is well-established in catalysis research, screening with respect to stability is experimentally difficult due to the long time scales of catalyst degradation. Computational catalyst screening can complement experimental studies aiming at the identification of new catalyst materials that are stable under operating conditions.

Experimental/methodology. In the HCl oxidation in the Deacon process using an oxide catalyst MO_x, the main catalyst degradation mechanisms are catalyst leaching in the form of volatile M-O-Cl compounds (see Figure), as well as bulk phase transformation of oxide catalysts into less catalytically active chlorides (see Figure). We present a catalyst screening approach based on experimental thermodynamic data for the compounds in the M-O-Cl system. In this approach, we divide the M-O-Cl system into four groups of compounds, oxides, chlorides, condensed and gaseous species and compute two descriptors .



Descriptor calculation for bulk chloride formation and leaching of volatile chlorides, and screening result displayed in the periodic table.

Results and discussion. It can address specific reaction conditions by computing the driving forces (ΔG) of chlorination and sublimation as a function of temperature, reactant feed composition and conversion. We apply it to the M-O-Cl compounds of 66 elements, regarding chlorination and volatility as separate descriptors. According to previous experimental studies, catalyst degradation starts at the reactor inlet and is driven by water formation [1]. At the target reaction conditions (T < 650 K, dry, $p(HCl)/p(O_2) \approx 1$, conversion < 1 %), the volatility and chlorination descriptors are largely complementary, which provides an explanation why it has historically been so difficult to identify stable catalyst materials for this reactions. However, 13 oxides and oxychlorides are identified as suitable candidates. While some of the candidates (TiO_2, ZrO_2, Al_2O_3, and SiO_2) are inactive (but already employed as catalyst supports in the Deacon process and known to be stable), other candidates are ruled out for safety concerns (BeO, ThO_2, UO_3). The most promising candidates are those exhibiting low volatility and medium propensity toward bulk chlorination. The results suggest that Nb_2O_5, Ta_2O_5, and the late rare earth oxychlorides (Dy, Ho, Er, Tm, Yb, Lu)OCl may be suitable catalyst materials for the Deacon process. [1]

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Influence of Water Vapor Treatment for NH_3-TPD on Solid Acid Catalysts

J. Adolphs[1*], Y. Konishi[2]

[1]*Microtrac Retsch GmbH, Haan, Germany*
[2]*MicrotracBEL Corp., Tokyo, Japan*
[*]*j.adolphs@microtrac.com*

Keywords: Ammonia TPD, solid acid catalysts, zeolites

Introduction

Temperature programmed desorption of ammonia (NH_3-TPD) is commonly used to evaluate the acidity (acid amount, acid strength) of solid acid catalysts such as zeolites. In many cases, there are two peaks, *l*-peak (low temperature) and *h*-peak (high temperature) in the TPD spectrum.

Experimental/methodology

The *l*-peak is derived from ammonia molecules which are adsorbed by hydrogen bonding on NH_4^+ cation on acid sites and is not considered to indicate the acidity. However, in the case of zeolites with weak acidity, such as Y-type zeolites, the *l*-peak and *h*-peak overlap, making it difficult to evaluate acidity. NH_3 TPD measurement with steam treatment is considered being effective to eliminate the *l*-peaks. In this contribution the procedure, and precautions are described. Ammonia as probe molecule is adsorbed onto the zeolite sample until it reaches equilibrium. Then the temperature of the sample is continuously increased, causing an enrichment with the desorbed molecules in the inert carrier gas (Helium). The standard TCD (Thermal Conductivity Detector) measures the total adsorbed amount and not the specific desorbed constituents. However, since zeolite adsorbs water in its pores, it is necessary to use a detector that can detect water and ammonia separately when measuring TPD. Also, since water vapor is introduced at high temperature, this method is not applicable to samples whose properties are changed by water vapor. Therefore, a quadrupole mass spectrometer is used to detect the desorbing ammonia at mass number 16. Mass number 17 was not used because the peak at 17 can be affected by the desorbed water.
NH_3-TPD measurements were performed under the following conditions.

Measuring equipment	: BELCAT II + BELMASS
Sample	: MFI, 50 mg
Temperature ramp rate and target temperature	: 10°C/min, 610°C
Adsorption gas	: NH_3/He 5%

According to Igi et al [1], in their experiments the steam treatment was performed by repeating the evacuation of the sample cell with following steam introduction. Differently, the catalyst analyzer BELCAT II is a dynamic flow type equipment operating permanent at atmospheric pressure. Fully saturated water vapor is generated by an advanced bubbling method with inert gas at room temperature under atmospheric pressure.

Results and discussion

The experimental results show that steam treatment eliminates the *l*-peak and leaves the *h*-peak shape almost unchanged, indicating that steam treatment in NH_3-TPD measurement is very effective for eliminating the *l*-peak and examining the *h*-peak in detail. To perform NH3-TPD measurement with BELCAT II, the vapor option and a quadrupole mass spectrometer BELMASS is necessary.

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Passivation and transfer of metal containing catalysts for *ex situ* characterisation

E. H. Wolf[1*], J. Schittkowski[1], D. Ramermann[1], J. Folke[1], W. Hetaba[1], R. Schlögl[1], H. Ruland[1]

[1]*Max-Planck-Institut für Chemische Energiekonversion, Mülheim, Germany*
[*]*elisabeth.wolf@cec.mpg.de*

Keywords: characterisation, passivation, methanol synthesis, ammonia synthesis

Introduction. To improve our knowledge of catalyst materials and their performance, it is crucial to characterise catalyst samples after testing them in a catalyic reaction. While it is preferable to investigate a catalyst *in operando*, this is not always a feasible option. Instead, a transfer of the materials to the characterisation setup, in air or in a controlled and inert atmosphere (e.g., a glove box), is often performed, or the catalyst may be passivated. However, this might change the properties of the samples, particularily in the case of metal catalysts. For this reason, careful attention has to be paid to the methods used for transferring activated catalysts from reactors to characterisation setups [1].

Experimental/methodology. We assessed Cu- and Fe-based catalysts used for the synthesis of methanol and ammonia, respectively [2,3], each after various methods of transferring the samples from the reactor to the characterisation setups. These methods included the inert transfer of the materials via a glove box, and various methods of passivation, applicable where an inert transfer is not feasible. The investigated passivation methods included treatments with dilute O_2 or dilute N_2O, as well as the gradual exposure of the samples to ambient air. As a control, an air flow was applied to some samples directly in the reactor. During the treatments in the reactor, the increase in temperature caused by the treatment was recorded. After the completion of the treatment, the materials were carefully characterised using various methods probing the entire sample (BET/BJH, XRD) or resulting in local sample information (TEM/EDX/EELS).

Results and discussion. Monitoring the increase in sample temperature as a result of the passivation treatment can provide an indication whether or not the passivation treatment was successful. The samples subjected to passivation treatments were partially oxidised to varying degrees depending on the treatment, as evidenced by spectroscopic and crystallographic analysis (EDX, EELS, and XRD). Despite this, the passivation treatments preserved other aspects of the samples, for example their mophology (Fig. 1), and can therefore be useful where it is impossible to inertly transfer samples to characterisation setups.

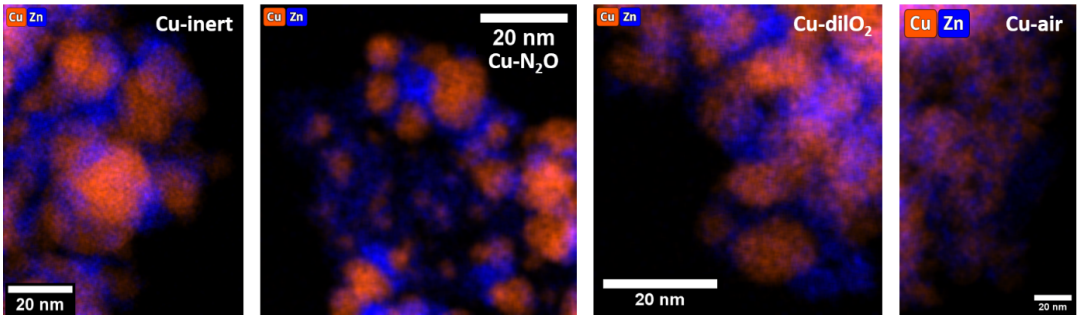

Figure 1: STEM-EDX Cu and Zn maps of a Cu-based methanol synthesis catalyst after various treatments.

Acknowledgments
We gratefully acknowledge the support received from the Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF, Verbundvorhaben Carbon2Chem, support code 03EW0004C) as well as the project partner Clariant for providing the catalysts. Furthermore, we wish to thank L. Kreutzheide, M. Heise-Podleska, A. Stoer and J. Taing for XRD and BET/BJH measurements as well as sample processing and -management.

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Operando XAFS/XES studies on Fe-containing zeolites to identify active sites for catalytic fast pyrolysis to fuels and chemicals

L.J.R. Higgins[1,2*], P.A. Wright[3], J.F.W. Mosselmans[1], A.M. Beale[2,4]

[1] Diamond Light Source Ltd., Harwell Science and Innovation Campus, Didcot, UK

[2] UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Oxford, UK

[3] EaStCHEM School of Chemistry, University of St Andrews, Purdie Building, North Haugh, St Andrews, UK

[4] Department of Chemistry, University College London, UK

[*] *luke.higgins@diamond.ac.uk*

Keywords: Catalytic Fast Pyrolysis, Fe-ZSM-5, XES, HERFD-XANES, Beamline I20 Diamond Light Source.

Introduction. Designing an effective, integarted biorefinery relies on developing robust processes for upgrading biomass to to fuels and chemicals [1]. This includes the production of high-value chemicals, such as benzene, toluene and xylene (BTX) from biomass. BTX are especially important as platform chemicals and are currently produced almost exclusively from fossil resources. A promising and well-developed process for producing BTX from biomass is Catalytic Fast Pyrolysis (CFP), during which pyrolysate vapour is upgraded into monoaromatic species using a catalyst. Zeolites such as ZSM-5 are known to be effective catalysts for hydrodeoxygenation of lignocellulosic biomass to high value BTX and monoaromatic hydrocarbons during CFP [2]. Recent research has shown that the addition of ca. 1 % wt. Fe to ZSM-5 has a notable impact on the selectivity of the reaction, typically increasing the BTX yields, when compared to non-Fe-modified zeolite [3]. It is believed that Fe sites in Fe-ZSM-5 zeolite are both selective and active towards monocyclic aromatic hydrocarbon (MAH) formation and suppress further polymerisation and the formation of oxygenates [4]. However, little is currently known about the mechanistic role of Fe in CFP.

Experimental/methodology. The aim of this project is to study the function of Fe during CFP of biomass. In the past, the study of these Fe sites has been challenging, due to the relatively low concentration (ca. 1.0 wt%) of Fe present in the zeolite. Modification of the zeolite using incipient wetness impregnation with Fe results in the formation of both mononuclear and polynuclear Fe sites (**Fig 1a**) [5]. This project exploits the recently commissioned 14 crystal analyser X-ray emission spectrometer at beamline I20 of Diamond Light Source (**Fig 1b**) to perform operando Resonant X-ray Emission Spectroscopy (RXES) and High Energy Resolution Fluorescence Detection (HERFD) X-ray absorption spectroscopy. The reaction was performed by injecting 1.5 µLmin^{-1} of a biomass model compound (furan) into a flowing stream of 30 mLmin^{-1} He gas) over 50 mg of the catalyst held at a series of temperatures and monitoring the evolution of BTX (**Fig 1c**). Fe K_β and valence-to-core emission spectra, as well as high energy resolution flouresence detection (HERFD) XANES were collected in-situ.

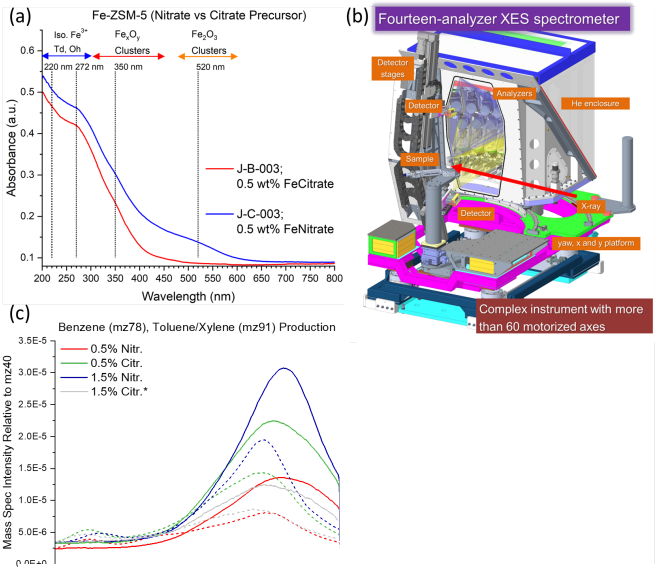

Figure SEQ Figure * ARABIC 1: (a) UV-Vis spectroscopy shows mononuclear and polynuclear Fe clusters present on modified ZSM-5 zeolite. (b) 14 analyser spectrometer at I20 DLS (c) Laboratory mass-spectrometry shows increasing evolution of BTX with higher Fe concentration.

Results and discussion. In this poster presentation, we present the recent advances made at beamline I20 as well as preliminary results showing changes in Fe speciation during CFP of furan over Fe-ZSM-5 catalysts. Initial results demonstrate significant mechanistic differences between plain ZSM-5 and Fe-ZSM-5, as well as pointing to changes in Fe speciation dependent on the intial distribution of mononuclear and polynuclear Fe sites.

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In-Situ Deactivation Measurements on bifunctional catayst for One-Step DME synthesis

Felix Hilfinger[1], Samuel F. Gatti[2] and Ingo Krossing[1]*

[1]*University of Freiburg, Material Research Center, Freiburg, Germany*
[2]*Paul Scherrer Institut, Villigen PSI, Switzerland*
[*]*ingo.krossing@ac.uni-freiburg.de*

Keywords: CO_2 Hydrogenation, DME Synthesis, DRIFTS, Catalyst Deactivation

Introduction. In recent years, the concentration of CO_2 in the atmosphere has been constantly increasing, having an impact on global climate change.[1] Therefore, a growing number of countries and researchers are interested in developing technologies to reduce CO_2 emissions and developing efficient carbon dioxide utilizations systems.[2] In the BioDME project, funded by the federal ministry of education and research Germany, we focus on developing a pilot plant for the hydrogenation of CO_2 to gain highly selective dimethyl ether (DME). The goal is further investigate the stability, economy and sustainability of this process in daily operation.[3] The direct synthesis of DME from CO_2 requires two catalyst parts: A metal oxide, usually Cu/ZnO/Al2O3 (CZA) or Cu/ZnO/ZrO2 (CZZ), for MeOH production, and a solid acid, usually zeolites like H-ZSM5, for the dehydration of MeOH to DME. Although, combination of the surface basic metal oxide and the acidic zeolite results in mutual deactivation, which limits the performance of the hybrid system. In this work, an all-new experiment to measure *in-situ* surface related deactivation of the acidic H-ZSM5 and the surface-basic CO_2 hydrogenation catalyst was developed. The underlying principle of the measurement is related to adsorption of pivalonitrile (PN) or acetonitrile (AN) on surface exclusive terminal silanol functions of H-ZSM5-type zeolites. These functional groups are strongly acidic and, due to their location on the surface, react with the surface-basic metal oxide. Therefore, the amount of residual silanol groups depends on the amount of deactivation or amount of surface-basic sites on the CO_2 hydrogenation component.

Experimental/methodology. Beside the house-made metal oxide CZZ, a commercial available H-ZSM5 zeolite was used and characterized by DRIFTS (*Diffuse Refelection Infrared Fourier Transform Spectroscopy*). Here, only the diffuse reflected part of the initial IR radiation is measured. Because of the low penetration depth of the diffuse reflected IR radiation, the DRIFTS method does not measure any bulk-related, but only surface related absorptions.[4]

Results and discussion. In Figure 1 the normalized raw spectra of different H-ZSM5 to CZZ ratios are shown. All of them resemble the expected bands at 3740 cm^{-1} with a negative intensity due to the perturbation of the SiOH-vibration introduced by PN adsorption. As expected, differential spectroscopy showed a decreasing area of the band assigned to surface exclusive terminal silanol groups at 3740 cm^{-1} with increasing CZZ content. Therefore, the deactivation of the acidic sites on the catalyst surface by the surface-basic metal oxide can be measured directly.

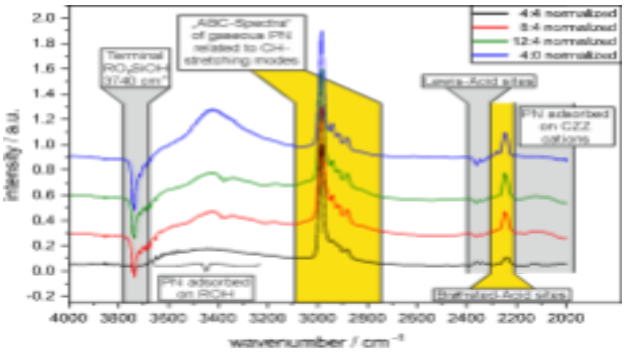

Figure 1: Differential DRIFTS-deactivation measure-n Figure ments for different H-ZSM5 to CZZ ratios in the range of 4000 cm^{-1} to 2000 cm^{-1}. Spectra normalized to the maximal intensity in the ABC-Spectra.[5-7]

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Isopotential Operando Spectroscopy – A New Concept for Operando Studies of Catalysts in Catalytic Reactors

B. Wollak[1], K. Bharatula[2], S.-F. Stahl[2], S. Sichert[1], O. Korup[1,2], R. Horn*[1,2]

[1]*Hamburg University of Technology, Hamburg, Germany*
[2]*Reacnostics GmbH, Hamburg, Germany*
*horn@tuhh.de

Keywords: operando spectroscopy, fixed-bed reactor, DRIFTS, Raman, XRD

Introduction. Operando spectroscopic measurements are traditionally conducted in miniature reactors by gathering spectroscopic data at defined temperatures, contact times and mixing patterns while simultaneously recording reactant conversion and product selectivity at the reactor outlet. Spectroscopic studies on catalysts directly in industrial reactors are almost not existing because industrial reactors are too large and opaque to electromagnetic radiation. Isopotential operando spectroscopy [1] is based on the hypothesis, that catalyst structure, adsorbates and reactivity are determined by the chemical potential of the reaction mixture the catalyst is exposed to ($\mu=\mu(T,p,\mathbf{x})$) and as such by temperature T, pressure p and local chemical composition **x** of the reaction mixture in the reactor. If the same catalyst, which is in the catalytic reactor, is put in a spectroscopic cell and is exposed to the same local chemical potential as in the reactor, the catalyst should display the same structure, adsorbates and reactivity as the catalyst locally in the reactor. This allows separating catalytic reactor and spectroscopic measurement cell, allowing to perform, at least in principle, operando spectroscopy inside industrial catalytic reactors. Any spectroscopic method can be used which is applicable for all T,p,**x** combinations encountered in the catalytic reactor. Because the spectroscopic cell must no longer serve simultaneously as catalytic reactor, it can be optimized from a spectroscopic point of view without any restrictions.

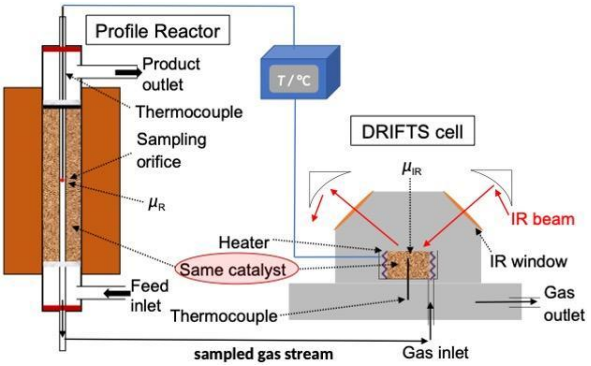
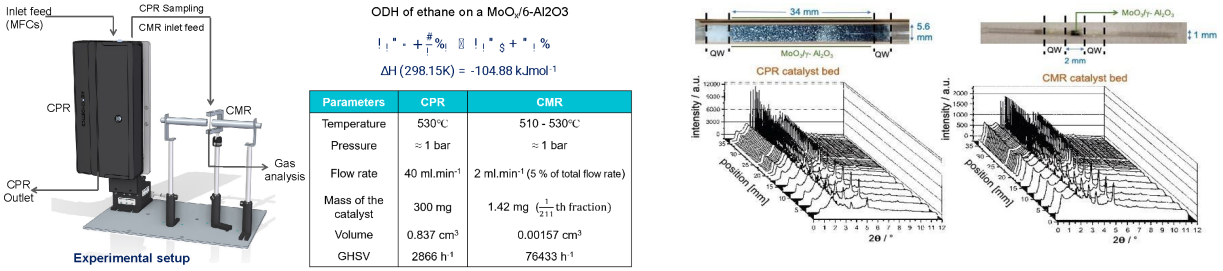


Fig. 1: Concept of isopotential DRIFTS spectroscopy.

Experimental/methodology. The present contribution demonstrates the concept of iso-potential operando spectroscopy by means of DRIFTS, Raman spectroscopy and XRD. Isopotential operando spectroscopic measurements are performed by equipping a catalytic reactor with spatial sampling and spatial temperature measurements and combining it directly with the spectroscopic measurement cell as shown schematically in Figure 1 for DRIFTS as example.

Results and discussion. Figure 2 shows exemplarily high energy (100 keV) XRD data of a MoO_x catalyst during ethane ODH measured at beamline P07 at PETRAIII/DESY. The reaction was performed in a Compact Profile Reactor (CPR). Spatial XRD patterns were recorded along the reactor by putting i) the CPR directly into the beam and ii) by putting a Capillary Micro Reactor (CMR) in the beam connected by isopotential coupling to the CPR and containing a small amount of the same catalyst as in the reactor. Almost identical XRD patterns and Mo reduction profiles were obtained.



Parameters	CPR	CMR
Temperature	530°C	510 - 530°C
Pressure	≈ 1 bar	≈ 1 bar
Flow rate	40 ml.min^{-1}	2 ml.min^{-1} (5 % of total flow rate)
Mass of the catalyst	300 mg	1.42 mg ($\frac{1}{211}$ th fraction)
Volume	0.837 cm^3	0.00157 cm^3
GHSV	2866 h^{-1}	76433 h^{-1}

Fig. 2: Spatial XRD profiles measured at beamline P07 at PETRAIII/DESY in a Compact Profile Reactor vs. those measured in a Capillary Micro Reactor connected in isopotential coupling to the CPR.

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Methane Pyrolysis on NiMo/MgO: Details of the Synergetic Effect

A. Horváth[1*], M. Németh[1], T.I. Korányi[1], A. Beck[1], Gy. Sáfrán[1], Zs.E. Horváth[1], I. Rigó[2]

[1]*Centre for Energy Research, Budapest, Hungary*
[2]*Wigner Research Centre for Physics, Budapest, Hungary*
[*]*horvath.anita@ek-cer.hu*

Introduction. Hydrogen may be an important energy source of our clean and sustainable future. For hydrogen production, the fossil natural gas-based steam reforming must be replaced with new routes that do not produce waste CO_2. A perspective way of CO_2-free utilization of abundant natural gas is the pyrolysis of methane ($CH_4 \rightleftharpoons C+2H_2$), yielding only pure H_2 and solid carbon. A very promising but less studied catalyst system for this reaction is composed of nickel and molybdenum, but the details of the prevailing bimetallic interactions need to be further clarified.

Experimental/methodology. MgO supported 7% Ni, 13% Mo and three bimetallic NiMo catalysts with high and low Mo content (~4% or 13%) were prepared by adsorption/precipitation of the metal precursors on MgO at room temperature or at 80°C, followed by washing, centrifugation, calcination at 550°C and reduction at 800°C. Samples are differentiated by the Mo/Ni atomic ratio (MoNi0.4 and MoNi1.2) and the synthesis temperature (MoNi0.4_RT). The bulk composition of the catalysts was determined by the ICP-OES method, the structure was characterized by transmission electron microscopy (TEM) and STEM-EDS studies, X-ray diffraction (XRD), temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The catalytic properties were determined a) in a MIC AutoChem device with QMS analysis using 1% CH_4/He flow with temperature ramp or at constant 700°C; and b) in a horizontal pyrolysis reactor with GC gas analysis using a 50% CH_4/Ar flow at 800°C. The amount of carbon produced after pyrolysis was determined by mass measurement or from the amount of decomposed methane, and its structure was analyzed by Raman spectroscopy and high-resolution TEM.

Results and discussion. According to the TPR results, the bimetallic samples could be fully reduced at around 800 °C, but in the case of the monometallic samples the reduction was not complete. The average metal particle size by TEM varied between 5 and 8 nm in all samples. The XRD indicated alloyed NiMo-particles for MoNi0.4 and MoNi0.4_RT catalysts, but for MoNi1.2 only the MgO reflections could be detected (finest dispersion). STEM-EDS showed that the larger bimetallic particles were always extremely rich in Ni, but areas with numerous smaller particles displayed higher Mo/Ni ratios different for each sample. According to the XPS, nickel has still 60% oxidic contribution in the reduced Ni/MgO and 20% in MoNi1.2 sample. Molybdenum is mainly metallic in Mo/MgO and MoNi1.2, but there is more Mo^{4+} present in the other two low-loaded bimetallic samples. It was also deduced from XPS that MoNi1.2 surface is enriched in Mo (Mo/Ni=1.7), while MoNi0.4 is depleted (Mo/Ni=0.2). In the temperature ramped CH_4 decomposition, Ni/MgO resulted constant 10% CH_4 conversion starting at 500 °C, Mo/MgO became steeply active only above 700 °C, while the bimetallic catalysts were active in both temperature ranges. In both, the AutoChem and the horizontal pyrolysis reactor, we found a synergistic effect of the bimetallic catalysts, and the MoNi1.2 sample was the best. According to the Raman and HRTEM results, the carbon formed on Ni/MgO was the most graphitic (I_G/I_D=7.7), while on Mo/MgO it was the most defective (I_G/I_D =0.4), just a few layer thick coverage around particles but resulted in rapid deactivation of both samples. On the best MoNi1.2 catalyst with 300% carbon yield, partially defective (I_G/I_D=3), multi-walled carbon nanotubes with a maximum diameter of 10 nm were obtained. The exceptional activity of the bimetallic MoNi1.2 sample can be explained by the high and stable dispersion of bimetallic NiMo particles with a special ~1:1 composition. This means that the interaction of Ni with sufficient Mo partners creates new active sites that allow the continuous carbon dissolution and nanotube formation, thus good catalytic performance during CH_4 decomposition.

Acknowledgments
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Probing the effect of electrolyte impurities on perovskite-based catalysts for electrochemical evolution of oxygen via *in-situ* Raman spectroscopy

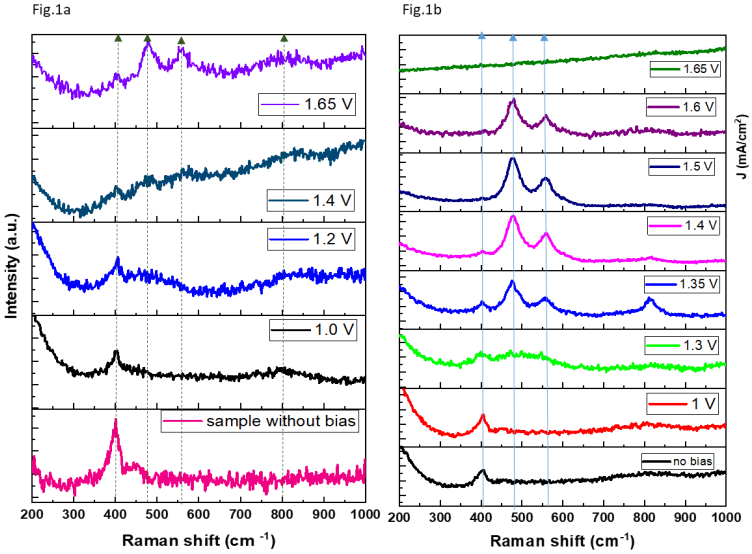
H. Cheraparambil*, Y. Wang, H. Tüysüz, C. Weidenthaler
Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany
* *cheraparambil@kofo.mpg.de*

Keywords: OER, Perovskites, Electrolyte impurities, Electrode-Electrolyte Interface, *In-situ* Raman studies

Introduction: Oxygen evolution reaction (OER) is the bottleneck of electrochemical water splitting[1] Therefore, intensive research is ongoing in developing efficient and low-cost catalysts, among which perovskites have demonstrated excellent OER activities.[2] Studies show that the catalytic performance is enhanced by Ni/Fe impurities present in the electrolyte. Nevertheless, the mechanism is still not completely understood.[3] Mixed Ni-Febased perovskites, $LaNi_xFe_{1-x}O_3$, also show catalytic enhancement for OER in the presence of electrolyte impurities for alkaline water electroylsis.

Experimental/methodology: Perovskites are synthesized via the modified solution combustion method. All samples have been investigated by electron microscopy and diffraction as well as Raman spectroscopy and X-ray photoelectron spectroscopy before and after OER. All samples are tested under alkaline OER conditions. The electrode-electrolyte interface is studied by operando Raman spectroscopy.

Results and discussion: $LaNiO_3$ shows the highest activity with an overpotential of 280 mV at a current density of 10 $mAcm^{-2}$ and excellent electrochemical stability after 15 h of testing. Rietveld analysis and Fourier difference analysis reveal a deviation from the perfect crystal structure and transmission electron microscopy confirms the presence of stacking faults which are correlated to the excellent OER performance. The electrocatalytic activity of Ni-Fe based perovskites is influenced by the impurities present in the alkaline electrolyte, 1M KOH (Fig.1c). For $LaNiO_3$, the active oxy-hydroxide species (around 477 and 555 cm^{-1}) are observed at the onset potential of OER in 1M commercial KOH. However with the addition of Fe impurities in the purified electrolyte the formation of the oxy-hydroxide species is observed at potentials as low as 1.35V. (Fig. 1a, 1b and 1d) Simiar trend is observed for $LaFeO_3$ in the presence of Ni impurities. In the mixed system, $La(NiFe)O_3$ as per the raman studies, nickel and iron atoms are the initial catalytic sites but at higher potentials Fe atoms significantly contribute to the active catalytic centers.



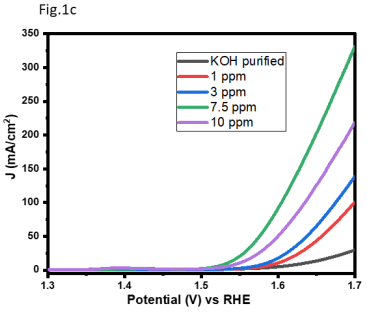


Fig.1d

Raman shift	Vibrational modes
~209	strucrural distortion
~400 ~451	Oxygen vibrations of the cage
~474 ~555	Bending and stretching modes of Ni-O in oxyhydroxide species
~825	Au-OOH*

Fig1: (a) In situ Raman studies on $LaNiO_3$ in 1M KOH; (b) in 1M KOH with Fe impurity (~7.5ppm); (c) Linear sweep voltammetry of $LaNiO_3$ in 1M KOH with different Fe impurity; (d) Table with different vibration modes

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Influence of Support Composition and Potassium Ion Doping on the Properties of Cerium-doped Zirconia Supported Silver Catalysts

Ewa Iwanek (nee Wilczkowska)[1*], A. Siwiec[1], S. Siennicka[1], and Z. Kaszkur[2]

[1]*Warsaw University of Technology, Warsaw, Poland*
[2]*Polish Academy of Sciences, Warsaw, Poland*
[*]*ewa.iwanek@pw.edu.pl*

Keywords: ceria-zirconia support, soot combution, solid solutions, potassium ions, ZrO_2 polymorphic forms

Introduction. Catalytic soot combustion is a reaction which is often carried out on a supported silver catalyst. It is known that potassium ions also catalyze the reaction. As in the case of coal gasification, the role of the catalyst is to enable oxygen to react with carbon to form CO_2. Although zirconium-ion doped ceria is often used a catalyst or a catalyst support, relatively little is known about the solid solutions in which a part of the zirconium ions have been substituted with cerium ions. Multicomponent supports have been rarely investigated in this reaction, hence the reported research investigated the various Ce/Zr ratios on the properties of the catalysts. The influence of the presence of potassium ions on the activity of such systems has been tested and presented herein.

Experimental/methodology. The supports were synthesized using co-precipitation using either zirconyl nitrate or zirconyl chloride and ammonium ceric nitrate mixed in the proper amounts to obtain solids with the compositions $Zr_{1-x}Ce_xO_2$ ($x<0.15$). Ammonia water (25%) was used as the precipitating agent. The formed gel was washed until a neutral pH of the filtrate was obtained, calcined at 550°C or 650°C in either air or argon for 4 h, crushed and sieved. The silver was deposited onto the grains of the supports using wet impregnation with silver nitrate to get a final loading of 1 wt.%, 5 wt.% and 10 wt.%. The catalyst precursor was then dried and calcined for another hour at 550°C. K_2CO_3 was deposited in the final step by wet impregnation. The catalysts were characterized by XRD, SEM-EDX, nitrogen physisorption, TPR, etc. Activity tests were carried out on an STA 449C thermobalance (NETZSCH) equipped with a mass spectrometer.

Results and discussion. The addition of the cerium ions led a higher surface area than that of undoped ZrO_2. The X-Ray diffraction results have shown that the cerium-doped zirconia supports crystallize solely in the tetragonal structure when the cerium ion content is 7at.% or higher. In contrast, when there is 3 or 5at%, the monoclinic ZrO_2 is also present. Its content was found to depend not only on the cerium ion content, but also on the calcination conditions, i.e., the temperature and atmosphere of calcination. An important finding was that the supports were found to exhibit reducibility, unlike undoped ZrO_2. The temperature of the beginnng of H_2 consumption was inversly correlated with the amount of monoclinic phase present in the support. The distribution of the silver was uniform in catalysts with 1wt% Ag (Figure 1a), whereas large crystals were observed when 5wt.% (or 10) was deposited onto the support (Figure 1b). The addition of K^+ was beneficial, especially for the systems with 1wt.%Ag.

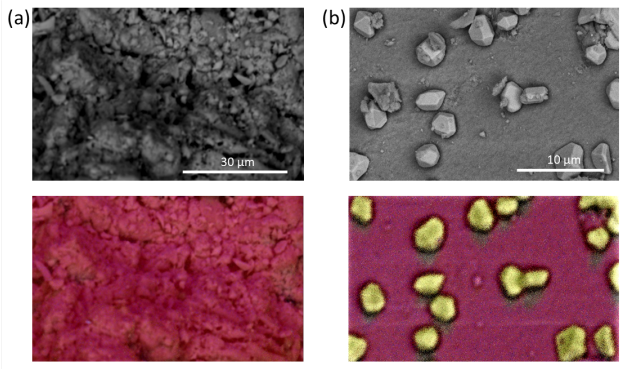

Figure 1. SEM images and the EDX color maps of (a) 1wt.%Ag and (b) 5wt.%Ag on $Zr_{0.90}Ce_{0.10}O_2$.

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Splitting of molecular oxygen for catalytic application

H. Jirglová[1*], E. Tabor[1], M. Lemishka[1,2], A. Kornas[1], K. Mlekodaj[1], J. E. Olszówka[1], J. Dědeček[1]

[1] *J. Heyrovský Institute of Physical Chemistry of the CAS, v. v. i., Prague, Czech Republic*
[2] *Faculty of Chemical Technology, University of Pardubice, Czech Republic*
[*] *hana.jirglova@jh-inst.cas.cz*

Keywords: Fe-FER, O_2 dissociation, alpha oxygen

Introduction. To oxidise hydrocarbons by O_2 its activation over heterogeneous catalysts is needed. Recently, it was found that iron ferrierite (Fe-FER) exhibited extraordinary properties toward O2 dissociation over binuclear cationic centres [1,2]. It was shown that the cooperation of divalent bare Fe located in β cationic positions of FER split O_2 and formed an active oxygen form $[Fe(IV)=O^{2-}]^{2+}$ (α-oxygen), which is used for further methane to methanol oxidation already at ambient conditions. In this work, we focused on the study of the oxidation properties of binuclear centres in methane oxidation at elevated temperatures.

Experimental/methodology. Iron was introduced to FER(Tosoh Corp., Si/Al 9) by impregnation method, in which organic medium was used as solvent. The Fe-FER prepared by this method with Fe/Al 0.08 was considered (due to the occupation of β cationic positions by Fe(II)) as a model material for studying the kinetics of the α-O formation by cleavage of O_2, its thermal stability, and reactivity in methane oxidation under in-situ conditions at 220 °C using FTIR and Mössbauer spectroscopy. The products of methane oxidation were analyzed by FTIR and mass spectrometry methods.

Results and discussion. FTIR and Mössbauer spectroscopy results confirmed that in studied Fe-FER sample, iron is mainly observed as divalent cations located in β cationic positions. This arrangement guarantee the formation of binuclear Fe(II) centres. Analysis of in-situ FTIR study recorded in O_2 flow shows that within interaction time 0 - 60 min the intensity of the band at 907 cm^{-1}, assigned to Fe(II) in β cationic position, decreases with increasing intensity of the band characteristic for the α-O at 897 cm^{-1} (Fig. 1a).[2] This correlation between decreasing concentration of β sites (band at 907 cm^{-1}), estimated from FTIR spectra, and formation of the band at 897 cm^{-1} are depicted in Fig. 1b. To oxidize all Fe(II) in β sites and to reach the highest intensity of the band typical for α-O the time of 60 min is required. Interaction of the α-O with CH_4 at 220 °C results in the instantaneous vanishing of the band at 897 cm^{-1}, and formation of the band at 907 cm^{-1} typical for Fe(II) siting in β position in FER. This result confirms that $[Fe(IV)=O]^{2+}$ is reduced by CH_4 with the restoration of Fe(II) species initially observed in the FTIR spectrum of evacuated Fe-FER. FTIR and mass spectrometry results confirmed the formation of methanol in the gas stream as products of the reaction of O_2 and CH_4 over Fe-FER at 220 °C. The results confirmed that the iron binuclear centres effectively split O_2 and transform methane to methanol at higher temperature (220 °C).

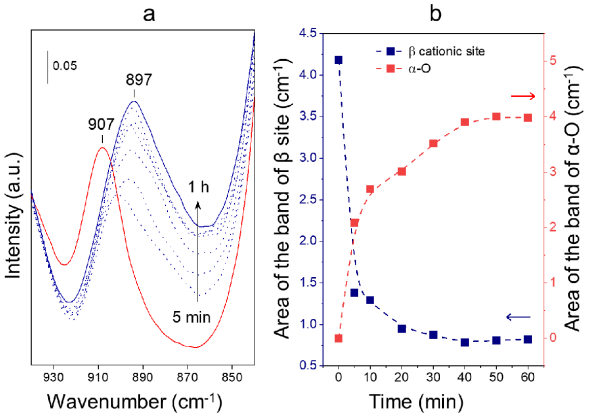

Figure 1. FTIR spectra of the kinetics of α-O formation over Fe-FER at 220 °C (a), and temperature dependence of the evolution of the bands characteristic for α-O and Fe(II) in β sites (b).

Acknowledgements

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Structural characterization of molecular organic frameworks and single atom catalysts for heterogeneous catalysis

I. Kappel[1,2*], M. Vennewald[2], R. Palkovits[2], C. Weidenthaler[1]

[1]*Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany*
[2]*RWTH Aachen University, Aachen, Germany*
[*]*kappel@kofo.mpg.de*

Keywords: Single-atom catalysis, Characterization

Introduction

Aiming at more sustainable chemical processes, the development of efficient catalysts plays a major role. In that context, the development of single-atom catalysts has a huge potential since they can bridge the gap between homogeneous and heterogeneous catalysis due to unique performance, better catalyst separation and handling as well as maximum metal utilization [1]. Single-atom heterogeneous catalysts (SAHCs) based on carbon-nitrogen polymers with low metal loadings have shown applicability for several catalytic systems [2,3]. However, the question arises whether the single-atoms are the active species in the reactions. Therefore, gaining a comprehensive structural understanding especially under reaction conditions is a key feature in order to be able to establish rational synthesis and treatment procedures for efficient SAHCs.

Experimental/methodology

We synthesized a palladium single-atom catalyst (0.5wt.%) on exfoliated gCN (ECN) by impregnation with $Pd(NH_3)_4(NO_3)_2$ (ECN-Pd-SA) as well as a palladium nanoparticle catalyst (ECN-Pd-NP). Both were tested towards their respective catalytic activity in ethylene hydrogenation. Aberration-corrected scanning transmission electron microscopy was used to analyse the catalysts before and after the catalytic reaction. *Ex-situ* and *in situ* X-ray photoelectron spectroscopy and X-ray absorption spectroscopy were applied in order to identify the active species. Furthermore*, ex-situ* and *in situ* synchrotron X-ray total scattering has been conducted to study both the structure of the ECN as well as a potential dynamic agglomeration process of the palladium single-atoms under reaction conditions.

Results and discussion

The conversion profiles revealed that the ECN-Pd-NP shows instantaneous activity at 50°C while the ECN-Pd-SA is inactive. Activation of the single-atom catalyst could be observed starting at 100°C and continuing with time and temperature. This activation could be attributed to an agglomeration of Pd single-atoms to clusters at 100°C in an atmosphere containing both hydrogen and ethylene [4].

However, due to the amorphous nature of the catalysts and the very low metal loading, the characterization comes with some challenges and is close to the detection limit of many techniques. Therefore, it is inevitable to apply multiple *ex-situ* and *in-situ* characterization techniques to both the polymeric support and the as-synthesized catalysts unravelling different detailed structural features and being able to derive valuable structure-property relationships.

Acknowledgments

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Effects of Hydrothermal Ageing on the Dynamic Nature of Active Sites in Cu-exchanged Small Pore Zeolites during NH_3-SCR

Rachit Khare[1*], Mirjam Wenig[1], Andreas Jentys[1], Johannes A. Lercher[1]

[1]*Department of Chemistry and Catalysis Research Center, Technical University of Munich, Garching*
[*]*rachit.khare@tum.de*

Keywords: NH_3-SCR, X-ray absorption spectroscopy, Operando characterization, DFT

Introduction. Cu-exchanged small-pore zeolites are currently the catalyst of choice for selective catalytic reduction of nitrogen oxides with ammonia (NH_3-SCR) owing to better hydrothermal stability and high catalytic activity across a wide range of temperature. During NH_3-SCR, Cu acts as a redox shuttle and exists in both Cu^{1+} and Cu^{2+} oxidation states coordinated either to the reactants or to the O atoms of the zeolite framework. The oxidation state and coordination environment of the active Cu species varies depending on the reaction conditions. During typical use, these catalysts are exposed to elevated temperatures in the presence of water resulting in a significant decrease in their catalytic activity over time. The decrease in the catalytic performance upon hydrothermal ageing is typically attributed to the changes in the coordination structure of active Cu species. However, the exact nature of this effect is still not fully understood. Utilizing *operando* X-ray absorption spectroscopy (XAS) supported with kinetic measurements and theoretical calculations, we present a comprehensive study elucidating the effects of hydrothermal ageing on the electronic and coordination structure of active sites in Cu-SSZ-13 and Cu-SSZ-39 during NH_3-SCR.

Experimental/methodology. SSZ-13 and SSZ-39 zeolites either were purchased commercially or were hydrothermally synthesized. The zeolites were ion-exchanged with aqueous copper acetate solution to achieve the desired Cu loading. The catalysts were hydrothermally aged by steaming at 1073 K for 16 h in 10% H_2O in synthetic air. *Operando* Cu K-edge XAS measurements were performed at the P64/P65 beamlines of the German electron synchrotron (DESY), while Al K-edge XAS measurements were performed at the Phoenix beamline of the Swiss Light Source (SLS).

Results and discussion. *Operando* Cu K-edge XANES and EXAFS measurements were performed on fresh and hydrothermally-aged zeolites under NH_3-SCR reaction conditions between 373 K and 823 K. Using principal component analysis (PCA), MCR-ALS analysis, and linear combination fitting (LCF), the distribution of Cu-species in the zeolites was expressed as a combination of four different components: (i) mobile Cu^{1+} coordinated to ammonia, (ii) mobile Cu^{2+} coordinated to ammonia, (iii) Cu^{1+} coordinated to the zeolite framework, and (iv) new Cu^{2+} species formed upon hydrothermal ageing (Figure 1). The fourth component was only observed in the hydrothermally aged zeolite samples. The identity of these principal components was verified both experimentally by exposing the catalyst to different gaseous mixtures and measuring the *in situ* X-ray absorption spectra and computationally by DFT calculations. The Cu^{2+} species formed upon hydrothermal ageing were shown to be primarily active for NH_3-oxidation, but not for NH_3-SCR, resulting in the decrease in the catalytic performance of hydrothermally ages zeolites, especially at high temperatures. Hydrothermal ageing also resulted in the formation of extra-framework Al (EFAl) as evidenced by Al K-edge XAS and ^{27}Al NMR. Formation of EFAl resulted in a partial collapse of the zeolite structure thereby imposing further mass transfer limitations within the zeolite pores. The structural stability varied as a function of zeolite framework; with AEI framework showing better hydrothermal stability compared to CHA. The Cu-ion and zeolite structure stability also varied systematically with Cu loading as well as with Si/Al.

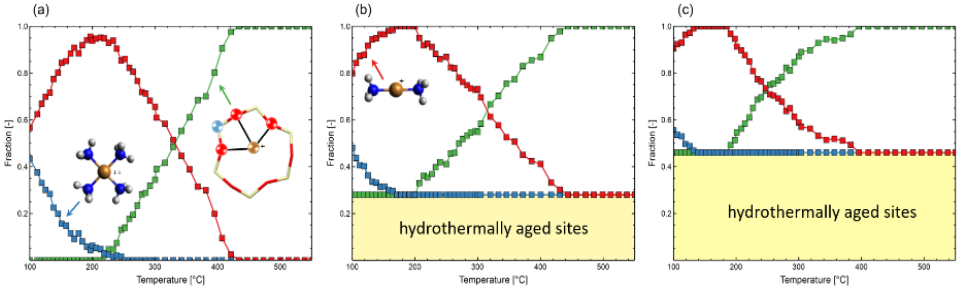

Figure 1. Distribution of identified Cu-species in Cu-SSZ-39 (a) and hydrothermally aged Cu-SSZ-39 (b) and Cu-SSZ-13 (c).

Epoxidation of light olefins on titanium silicate catalyst

[1]M. Alvear, [1]Kari Eränen, [1]Dmitry Murzin, [1]N. Kumar, [1]Tapio Salmi
[1]Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi, FI-20500 Turku/Åbo, Finland.
e-mail: matias.alvear@abo.fi

Keywords: epoxidation, hydrogen peroxide, titanium silicate and trickle-bed reactor.

Introduction. Since the discovery of titanium silicate more than 40 years ago, the epoxidation of propylene to propylene oxide with hydrogen peroxide has experienced of new technologies to produce this useful chemical compound. However, the commercial TS-1 catalyst used in methanol solvent gives methoxy species and glycols as secondary ring-opening products which are formed from the epoxide. The study of titanium silicate has brought up many new catalyst modifications. Nevertheless, the most promising one is Ti-MWW. The present work search to understand the differences between these two materials, TS-1 and Ti-MWW. TS-1 is more active in methanol, while, Ti-MWW is more active in acetonitrile.

Experimental/methodology. The laboratory-scale apparatus consisted of two main parts, a trickle bed reactor and a gas chromatograph. Solid titanium silicate catalyst TS-1 (ACS Materials, specific surface area 400 m^2/g, SiO_2:TiO_2>25) or Ti-MWW (in-house hydrothermally synthesized, specific surface area 485 m^2/g, SiO_2:TiO_2>20) particles (125-355 micrometer) were placed in the trickle bed between two sections of inert material [1-3]. In the laboratory-scale reactor, the aim was to compare the behaviors of both catalysts and the effect of the different process parameters on the product selectivity and reactant conversion. The FT-IR spectroscopic study comprised modulation excitation experiments. The effect of the modulation of a high and a low concentration over a ZnCe crystal with a layer of a catalyst was studied in these experiments.

Results and discussion. The reactor level results suggested important differences between both catalysts, nonetheless, both catalysts were highly active and selective in the epoxidation process. TS-1 displayed to be more active, however, the epoxide selectivities were lower than for Ti-MWW. The increase in the temperature displayed to be positive for Ti-MWW increasing the activity without decreasing the selectivity below 99%. Nevertheless, under similar conditions TS-1 exhibited to generate high concentrations of by-products and the catalyst activity decreased with the time-on-stream.

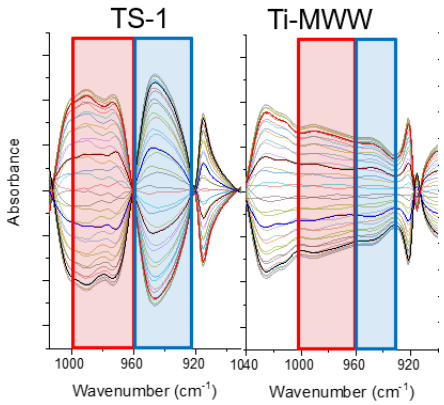

Figure 1. Modulation of water in acetonitrile, at 30 C.

The modulation excitation spectroscopy is a powerful tool to observe the presence of active surface species in the reaction system. During this work the study of the 960 cm^{-1} delivered important insights. The interaction of the framework titanium with the water displayed to be different for the catalyst materials investigated. Figure 1 reveals the differences between the responses. TS-1 exhibited important changes in the structure of the 960 cm^{-1} signal, while Ti-MWW displayed to not be highly excited by the water concentration.

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Catalyst materials characterization by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

M.Kleine-Boymann[1*], Sven Kayser, Julia Zakel

[1]*IONTOF GmbH, Muenster, Germany*
[*]*matthias.kleine-boymann@iontof.com*

Keywords: TOF-SIMS, surface analysis, interface analysis, elemental and molecular mapping

Introduction. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a technique that has many properties that are well-suited to catalysis research, but it is not yet well-established as a standard technique for the analysis of heterogeneous and homogeneous catalysts. This may be because ToF-SIMS operates in ultra-high vacuum, is generally a semi-quantitative technique, and generates complex spectra. However, the technique's unique properties offer multiple opportunities for ToF-SIMS in the field of catalysis research, such as

- very shallow sampling depth (approximately 1 nm),
- sub-ppm detection limits,
- elemental and molecular information,
- parallel mass detection in all operation modes,
- sub 100 nm lateral resolution for elemental and molecular mapping,
- sputter profiles with high depth resolution (less than 1 nm).

In synthesis and subsequent characterization, features like trace element detection and high lateral resolution can be applied to study the quality of synthesized materials in the form of powders, as well as model catalyst systems like thin films. This method is not limited to inorganic substances and is also applicable for biocatalyst research.[1–5]

Experimental/methodology. ToF-SIMS data shown in this presentation were acquired on different instruments, often without any sample preparation after transport through air. Powder samples are typically compacted for easy analysis by limiting the topography and the mobility of individual particles under ion bombardment.
We have studied the existing literature on ToF-SIMS applied to catalysis materials and analysed common approaches. We will illustrate the features and limitations in the field of catalysis using examples from the literature and some original data acquired in collaboration with academic partners.

Results and discussion. Our study shows that ToF-SIMS is indeed applicable to a wide range of catalyst materials and research questions, especially when combined with other techniques like LEIS, XPS, or SEM/EDS to supplement and complement the limitations in quantification inherent in ToF-SIMS. The rich information in the spectra is often used to prove the selective presence of a metal on a distinct phase of a mixed support. The high lateral resolution is, for example, used to assess the homogeneity of the material, probe three-phase boundaries or other active sites. Furthermore, the excellent detection sensitivity is utilized when looking at materials with very low loading, contamination, or residues from the synthesis or use of the catalyst and their impact on material performance.

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Catalytic behaviour of boron based materials in propane ODH

Kateřina Knotková[1*], Mehran Sajad[1], Roman Bulánek[1]

[1*] *Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic*

Keywords: ODH, propane, boron, silica, alumina

Introduction. Catalytic activity of boron oxide supported by different supports has been studied in oxidative dehydrogenation of light alkanes (ethane, propane) since early nineties [1]. After ten years the interest in boron oxide-based catalysts decreased due to mediocre results but it was revived by Grant et al. in 2016 by presenting data concerning exceptional catalytic activity of hexagonal boron nitride (h-BN) in ODH of propane [2]. In this work, Grant et al. showed extraordinary selectivity of h-BN to olefins (propene + ethene) of 91 % at a conversion of 14 % and only negligible losses of hydrocarbon by over-oxidation to CO_2. Similar catalytic behavior has also been observed for various boron binary compounds and even elemental boron itself. In all cases, partial oxidation of the catalysts and formation of BO_x groups was observed. The presence of these functionalities is considered to be responsible for the catalytic activity. This claim was proved by the synthesis of silica-supported boron oxide by incipient wetness impregnation. [3,4] However, BO_x-SiO_2 catalysts suffered from significant boron leaching from the catalyst surface under reaction conditions. Thus, the question of the nature of the active center, the role of boron speciation, the influence of the support and the stabilization of BO_x groups on the surface of the support still remains unsolved. In our study we have compared catalytic behaviour of h-BN, BO_x-SiO_2 and BO_x- γ-Al_2O_3 and studiedproperties of boron particles present on the catalyst surfaces.

Experimental/methodology. Supported BO_x-SiO_2 and BO_x- γ-Al_2O_3 catalysts were prepared by impregnation method using triisopropyl borate (for synthesis, Sigma Aldrich) as the boron source. h-BN was purchased from Sigma Aldrich. The prepared catalysts were characterized by FTIR, Raman, XPS and XRD techniques. The catalytic test were performed using 100 mg of catalyst in total flow 20 ml/min and reaction mixture molar composition $C_3H_8/O_2/He$ = 6/3/11.

Results and discussion. There were prepared by the same procedure alumina- and silica- supported boron catalysts with low (0.2 wt. %), and high (2.4 wt. %) boron content. FT-IR and Raman spectroscopy revealed intensive sharp bands ~ 1380 cm^{-1} and bands at ~1060 and ~1170 cm^{-1} belonging to B-O from different boron-oxo species like boric oxide, metaborates and boroxol rings, respectively. Powder XRD confirmed presence of larger nanoclusters of B_2O_3 on silica support with the highest concentration of boron and on spent h-BN catalyst. XPS spectroscopy demonstrated that boron species are stable on alumina surface on the contrary to silica and that BO_x species on h-BN are formed at expense of nitrogen. Activity and selectivity over individual catalysts differed in propane ODH. However, it can be stated that all three types of catalysts were dominated by olefins with a selectivity between 71 and 88% (propene, ethene), followed by CO (10-20%) and methane (0-5%). BO_x-SiO_2 showed the highest selectivity to olefins catalyst, the BO_x-Al_2O_3 system showed the highest ratio between C3 and C2 olefins. With increasing propane conversion, the overall selectivity to olefins decreased slightly and the relative content of ethene increased, more significantly on silica than on alumina. The obtained results prove that the stability of BO_x species and at least the selectivity of ODH propane can be influenced by the character of the support. A more basic support stabilizes the surface BO_x species more effectively and maintains a higher selectivity to propene. On the other hand, Al_2O_3 itself exhibits catalytic activity leading to the production of oxygenates and C4 hydrocarbons as by-products.

Acknowledgments

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Understanding the mechanism of preparative green MOF-74 syntheses using *operando* ATR-IR spectroscopy

I. Kochetygov[1], M. Ranocchiari[1], D. Ferri[1*]

[1]*Paul Scherrer Institut, 5232 Villigen, Switzerland*
[*]*davide.ferri@psi.ch*

Keywords: operando spectroscopy, synthesis, metal-organic framework

Introduction. Metal-organic frameworks (MOFs) show great promise among nano- and micro-porous materials due to their intrinsic tunability and structural versatility, leading to their use in numerous applications in catalysis.[1] While the MOF field offers a great choice of materials after more than 30 years of development, one of the remaining challenges for their real-world implementation is the development of reliable synthetic procedures with speed, scale, and quality matching the industry requirements. Recently, aqueous-based room-temperature syntheses of certain MOFs, such as MOF-74/CPO-27 analogs were developed, allowing outstanding space-time yields of up to 18 720 kg m^{-3} day^{-1}.[2] These green, high-yielding methods produce minimal waste and are promising for large-scale MOF implementation. However, there is a lack of understanding of the underlying mechanisms, which is crucial for further extension and optimization to other MOF families and the fundamental understanding of MOF formation pathways. In this work, we study the mechanism of the MOF-74 family formation in aqueous solutions on a preparative scale (> 0.5 g).

Experimental/methodology. *Operando* Attenuated Total Reflection IR spectroscopy (ATR-IR) was employed to study the mechanism of the MOF-74 family formation in an aqueous solution using a custom-made stainless steel batch reactor cell equipped with a ZnSe crystal (30°, 50x44x2 mm). Multivariate curve resolution-alternating non-negatively constrained least squares (MCR-AR-NNLS, as implemented in the pyMCR package)[3] of the ATR-FTIR data was utilized to extract the kinetic profiles of the species in the reaction mixture. The reaction products of the synthesis in the spectroscopy cell were isolated and characterized using powder X-ray diffraction, thermogravimetric analysis, and nitrogen physisorption.

Results and discussion. To study the proceeding of the synthesis, the solution of the sodium salt of 2,5-dihydroxyterephthalic acid was added using a syringe to the stirred solution of the Zn precursor in the ATR-IR cell. The reaction of MOF synthesis was found to proceed via the formation of an intermediate, which contains a twice-deprotonated ligand molecule (Figure 1). However, the nature and presence of the intermediate depend on the metal ion used in the synthesis. The kinetics of the MOF formation was also found to depend on the nature of the MOF metal ion and the synthesis temperature. The reaction products of the synthesis in the spectroscopy cell were pure MOFs and their excellent quality was confirmed by their conformity to the expected crystal structure and high BET surface area values exceeding 1350 m^2g^{-1}. Last, using the information revealed during the *operando* study, optimized synthetic protocols for MOF-74 materials are proposed.

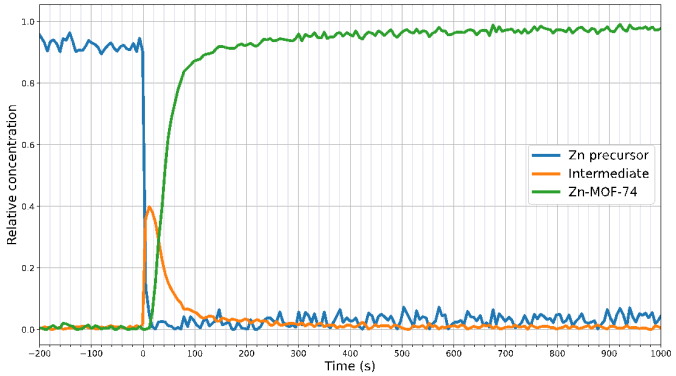

Figure 1. Typical MCR results for a Zn-MOF-74 synthesis followed by *operando* ATR-IR

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Genesis of Cuprous Acetylide Cu_2C_2 as Active Species for Reppe Ethynylation of Formaldehyde

Lingdi Kong[1*], Franz Bannert[1], Klaus Köhler[1],
Andreas Reitzmann[2], Roman Bobka[2], Dennis Beierlein[2]

[1] *Department of Chemistry and Catalysis Research Center, Technical University of Munich Lichtenbergstr. 4, Ernst-Otto-Fischer-Str. 2, 85748 Garching, Germany*
[2] *BU Catalyst, Clariant Produkte (Deutschland) GmbH, Waldheimer Straße 13, 83052 Bruckmühl, Germany*
[*] *lingdi.kong@tum.de*

Keywords: Acetylene, Cuprous acetylide, Ethynylation, Formaldehyde, Reppe chemistry

Introduction

In the 1940's Walter Reppe initiated the use of acetylene as raw material in industrial processes.[1] Today, the catalytic Reppe ethynylation reaction of acetylene and formaldedhyde to produce 1,4-butynediol represents an important C4 feedstock for high value-added downstream chemicals. The generally accepted catalytically active species in this reaction, cuprous acetylide, Cu_2C_2, has been experimentally identified only recently, probably due to its complex structure and explosive nature.[2]

Necessary safety precautions for handling of cuprous acetylides make analytical characterization very challenging. Motivated by Bruhm et al.,[2] who successfully identified Cu_2C_2 formed from copper oxide pre-catalysts, the formation of Cu_2C_2 during typical industrially applied catalyst activation procedures has been followed (pseudo) in situ in the present contribution. Particular safety protocols have been worked out and applied. Unsupported Cu_2C_2 model compounds were also synthesized for comparison.

Experimental/methodology

The synthesis of silica supported copper(II)oxide catalyst precursors was performed by co-precipitation followed by calcineation at 450°C. Activation is carried out under typical ethynylation conditions in formaldehyde solution at 1.2 bar acetylene and 90°C. The activated catalysts (wet, slurry) is analyzed by powder-XRD and Raman spectroscopy. The Cu_2C_2 quantity is deduced from thermal analysis.

Results and discussion

The mechanism of catalyst activation and formation of the active phase cuprous acetylide on silica could be deduced from the influence of various activation parameters as pH value/buffer systems, reducing agents, reactant concentrations, temperatures and additives. Thus, e.g. the Cu(II) precursor is not reduced by formaldehyde alone as generally assumed in the literature up to now. The formation of the catalytically active phase invloves CuO dissolution and Cu_2C_2 re-deposition steps. A p-XRD diffractogram of a slurry of an activated catalyst is shown in Figure 1. All activated catalysts were evaluated according to their performance in the ethynylation of HCHO to 1,4-butynediol.

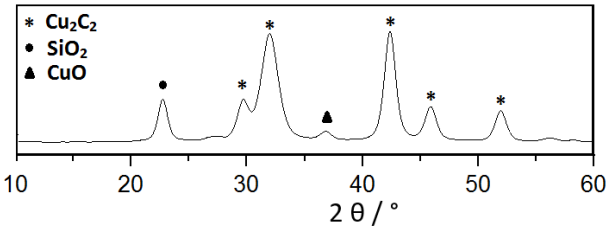

Figure 1. Powder-XRD diffractogram of a silica supported copper oxide pre-catalyst activated under ethynylation reaction conditions. Reflexes of Cu_2C_2 and other components are assigned from crystalline Cu_2C_2 model compounds and reference data published by Bruhm et al.[2].

Acknowledgments

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The functionality of binuclear centres in CHA in the dissociation of molecular oxygen

A. Kornas[1*], K. Mlekodaj[1], E. Tabor[1], D. K. Wierzbicki[2], S. Sklenak[1], H. Jirglová[1], J. Dědeček[1]

[1] *J. Heyrovský Institute of Physical Chemistry of the CAS, v. v. i., Prague, Czech Republic*
[2]*Paul Scherrer Institut, Villigen, Switzerland*
**agnieszka.kornas@jh-inst.cas.cz*

Keywords: binuclear centres, alpha oxygen, Fe-CHA

Introduction. A recent study showed that binuclear Fe(II) sites in zeolite of FER topology exhibit the unique ability to split molecular oxygen with the formation of α-oxygen species. Formed α-oxygen possesses an outstanding activity in the oxidation of CH_4 already at ambient temperature. Moreover, the products of this reaction were detected in the gas stream without an additional extraction step [1]. According to the current state of art, to form binuclear sites in the zeolitic matrix, a high population of closely located Al atoms (Al pairs), which stabilize divalent cations is required, as well as an axial geometry of two the cationic sites distanced by ~7Å. [1,2] However, this structural condition strongly limits the variety of zeolitic topologies efficient in the activation of O_2. The aim of this contribution was to investigate the ability of zeolites with non-axial coordination of Fe(II) sites to split O_2 and subsequently oxidize CH_4. For the study zeolite of CHA topology was chosen due to its low Si/Al guaranteeing a high population of Al pairs, enhancing the potential formation of binuclear sites, and sufficient distance and arrangement iron sites to activate molecura oxygen.

Experimental/methodology. DFT calculations (VASP program) including molecular dynamics were used to verify the possibility of O_2 splitting over iron sites in zeolites of CHA topology. CHA sample (Si/Al 2.1) was synthesized with the template-free procedure [3], and iron was introduced to the sample by the impregnation with an acetylacetonate solution of $FeCl_3$. Mössbauer and XAS spectroscopies were used to study the speciation and redox properties of iron sites after the evacuation of the zeolite at 450 °C, interaction with O_2, and subsequent reaction with CH_4 (as a testing reaction) at moderated temperatures (RT-220 °C). The activity tests in CH_4 oxidation were performed at various oxidation times and temperatures in three consecutive redox cycles with mass spectrometry detection of the reaction products.

Results and discussion. Synthetized sample CHA sample possesses typical structural parameters for zeolite of CHA topology (XRD, SEM), and the exclusive presence of framework Al atoms (^{27}Al MAS NMR). Mössbauer and XAS studies of evacuated Fe-CHA confirmed thepresence of atomically dispersed Fe(II) cations. Obtained spectral characteristics confirmed that the interaction of iron sites in CHA with O_2 led to the oxidation of iron Fe(II) $\rightarrow$(Fe(IV)=O)$^{2+}$, which was subsequently reduced to Fe(II) by CH_4. The analysis of the oxidation products revealed the presence of CO_2 and methanol detected directly in the gas stream. Moreover, the Fe-CHA works effectively in three consecutive reaction cycles. Gathered data allows the selection of optimal reaction conditions in order to obtain the highest productivity of oxygenates.

The results of this pioneering study confirm that O_2 can be efficiently activated over binuclear iron sites in CHA and further applied for the oxidation of such inert molecule as CH_4. Despite carrying the reaction over narrow-pored CHA topology, the oxidation products desorbed spontaneously from zeolite channels.

Acknowledgments

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The role of metal-support interactions in shape-controlled TiO_2 systems for photocatalytic hydrogen evolution

Elizaveta Kozyr,[1*] Francesco Pellegrino,[1] Silvia Bordiga,[1] Elena Groppo,[1] Aram Bugaev,[2] Lorenzo Mino[1]

[1]*Department of Chemistry and NIS Centre, University of Torino, Turin, Italy*
[2]*SuperXAS beamline, SLS, Paul Scherrer Institute, Villigen, Switzerland*
[*]*elizaveta.kozyr@unito.it*

Keywords: *operando* spectroscopy, shape-controlled nanoparticles, XAS spectroscopy, photocatalysis.

Introduction.

One of the alternatives for future energy sources is hydrogen. This energy resource is attractive due to the possibility of obtaining it through green and renewable processes [1], such as photocatalytic water splitting. Noble metal nanoparticles (NPs) deposited on TiO_2 are among the most active systems for this reaction [2]. The rational design of a photocatalyst requires a detailed understanding of the relationship between structure and activity. In particular, the role of the different exposed TiO_2 surfaces and the chemical states of the supported metal NPs during the hydrogen evolution reaction needs to be clarified.

Combining multiple spectroscopic techniques in one experimental setup provides the possibility to look at catalytic systems from different perspectives and get comprehensive information.

Experimental/methodology.

We have investigated Pd NPs deposited on TiO_2 by photodeposition or deposition-precipitation techniques. To reveal the effect of metal-support interaction on the NPs reactivity we chose different TiO_2 morphologies, namely P25 and nanosheets. The catalyst was loaded inside a home-made cell, allowing to collect simultaneously also X-ray absorption spectroscopy (XAS), UV-Vis and mass spectrometry data. Pd *K*-edge XAS spectra were collected *in situ* during photodeposition of Pd on TiO_2 and subsequent hydrogen evolution reaction in liuid phase and in gas phase upon exposure to H_2 and O_2. UV-Vis spectra were collected *in situ* using Ocean optics and *ex situ* at different stages of the photodeposition. FTIR spectra using carbon monoxide as probe molecule were also measured in situ to assess the oxidation state and coordination of the surface exposed sites.

Results and discussion.

Operando XAS and UV-Vis spectroscopies revealed the reduction of Pd species during photodeposition from Pd(II) precursor to Pd(0) nanoaprticles acompained with the growing signal of the produced H_2. The redox properties of the formed metal NPs were probed in situ by exposure to molecular O_2 and H_2. Both morphologies with photodeposited metal on TiO_2 had stable Pd(0) NPs even at high tempertures in O_2 atmosphere, while samples obtained by the deposition-precipitation method were easily oxidized to Pd(II) oxide. Weak signal detected in difference XAS spectra suggested only surface Pd-O_2 interaction, which was stronger for Pd/TiO_2 nanosheets in comparison with Pd/TiO_2 P25. This was explained by stronger metal-support interaction in the case of {101} facets of TiO_2, dominating in P25, compared to the {001} ones, dominating in the nanosheets. Similar reactivity was proved by *in situ* IR spectroscopy using CO as a probe on the samples treated both under oxidizing and reducing conditions. FTIR spectra for CO adsorbed on Pd/TiO_2 samples after oxidation at 400°C shows two peaks at about 2120 cm^{-1} and 2100 cm^{-1} is due to to two contribution CO on ionic Pd^+ and CO on metallic Pd respectively, and CO absorption on Pd^{2+} ion leads to the appearance of a band at 2160 cm^{-1}.

In conclusion, we succesfully performed a multi-technique in situ investigation to follow the evolution of active Pd sites in the Pd/TiO2 catalyst and highlight the role of the metal-support interactions as a function of the TiO_2 morphology and of the metal deposition method, allowing to correlate the catalyst structure with its photocatalytic properties.

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Effect of H_2O Pre-exposure on CH_4 Oxidation and Passive NO_x Adsorption Performance over Pd/zeolite Catalysts

Tala Mon, Jacob Concolino, Junjie Chen, Eleni A. Kyriakidou*

Chemical and Biological Engineering Department, University at Buffalo, The State University of New York, Buffalo, NY 14260 (USA)
**elenikyr@buffalo.edu*

Keywords: Pd/zeolite, CH_4 oxidation, passive NO_x adsoprtion

Introduction: Pd speciation is essential to the investigation of Pd-based zeolite catalysts for passive NO_x adsorption (PNA) and methane (CH_4) oxidation catalysts applications with ion-exchanged Pd^{2+} and PdO nanoparticles as the active sites, respectively. The factors governing Pd speciation determine how Pd/zeolite catalysts should be stored and what pretreatments are required to restore the catalyst before use for PNA and CH_4 oxidation applications. Herein, the effect of H_2O pre-exposure on Pd speciation in 0.5 wt.% Pd/BEA and Pd/CHA is investigated at ambient temperature (25 °C) with ambient moisture (3.1% H_2O). PNA and CH_4 oxidation evaluations are used as probe reactions to determine the presence of Pd^{2+} and PdO species, respectively, before (fresh) and after H_2O pre-exposure.

Experimental/methodology: NH_4-BEA (Si/Al = 12.5) (Zeolyst) were calcined at 500 °C/2 h to form H-BEA (12.5). Na-CHA (11) was synthesized as reported previously and was ion exchanged 3 times with 1 M NH_4NO_3 (80 °C/8 h), dried (110 °C/8 h), and calcined (550 °C/8 h) to produce H-CHA [2]. 0.5 wt.% Pd/BEA and Pd/CHA were synthesized by incipient wetness impregnation. The final catalyst was dried (110 °C/8 h) and calcined (500 °C/2 h). The CH_4 oxidation (1500 ppm CH_4, 12% O_2/Ar, 100 - 600 °C (5 °C/min)) and PNA (100 ppm NO, 12% O_2/Ar, adsorption: 100 °C/30 min) performance of the synthesized catalysts were evaluated in a packed bed micro-reactor (100 mg (250-500 µm), 333 sccm, 200 L g^{-1} h^{-1}, pretreatment: 750 °C/1 h (20% O_2/Ar)). The catalysts were pre-exposed to 3.1% H_2O, 20% O_2/Ar at 25 °C/4 h for investigating the effect of H_2O on Pd speciation. The presence of ionic Pd was determined by NO and CO diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

Results and discussion: Small pore Pd/CHA (69%) outperformed large pore Pd/BEA (13%) as fresh catalysts at 600 °C suggesting the presence of more PdO in Pd/CHA compared to Pd/BEA (**Fig. 1A**). The CH_4 conversion of Pd/BEA was drastically improved after H_2O pre-exposure from 13% to 98% at 600 °C with Pd/CHA (from 69% to 87%) improving less in comparison to Pd/BEA. NO-DRIFTS showed a decrease in ionic Pd(NO) (1875, 1845 cm^{-1}) after H_2O pre-exposure over Pd/BEA suggesting that solvation of ionic Pd to form PdO may be responsible for the improved CH_4 conversion compared to the fresh Pd/BEA (**Fig.1B**).

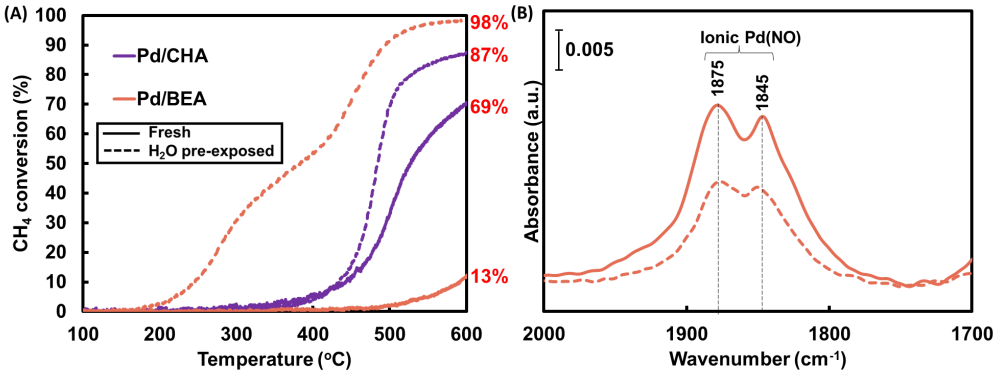

Figure 1. (A) CH_4 oxidation light-off curves of fresh (solid line) and H_2O pre-exposed (dashed line) Pd/BEA and Pd/CHA and (B) NO-DRIFTS of Pd/BEA.

Acknowledgments

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Uncovering Active Site Deactivation Dynamics in the Industrial Decomposition of N_2O through Operando Infrared Spectroscopy

M. Laluc[1*]; A. Lahougue[1]; E Rohart[1]; A Garbujo[2]; P Biasi[2]; P Bazin[3] ; M Daturi[3]

[1]*Alsys, Ploemeur, France*
[2]*Casale SA, Lugano, Switzerland*
[3]*LCS-ENSICAEN-UNICAEN-CNRS, Caen, France*
[*]*Corresponding Author's E-mail address : mathias.laluc@alsys-group.com*

Keywords: Operando FTIR, Active site, Fe-FER, N_2O decomposition

Introduction.

Nitrous oxide N_2O is considered one of the major pollutants, the third one after carbon dioxide CO_2, and methane CH_4. N_2O has a global warming potential around 300 times higher than CO_2, and like CO_2 it is long-lived spending an average of 120 years in the sky before disintegrating. In this context of global warming, continued interest in developing and understanding N_2O decomposition is growing.

Reducing N_2O emissions from industrial processes is a complex challenge. Low-temperature processes are being explored to minimize energy costs, while efforts are also being made to improve catalyst performance in the presence of different molecules contained in the industrial flow, such as O_2, NO, NO_2, CO_2, and H_2O, which can negatively impact catalyst activity or cause deactivation. According to the literature, Fe-FER and Fe-ZSM-5 catalysts have demonstrated the best results, with Fe-FER exhibiting superior activity in the presence of NO. Despite these efforts, the underlying mechanisms and key factors driving N_2O decomposition remain uncertain and open to debate.

Experimental/methodology.

Operando FTIR spectroscopic techniques lead to providing further insight into N_2O decomposition. In this work, different catalysts such as Fe-FER and Fe-ZSM-5 were studied. Industrial conditions were simulated (gas mixtures with N_2O, O_2, H_2O, etc.) working under pressure and adding different activity promoters, such as NO, CO, and CH_4 to the mixture. In addition, isotopic substitutions were used to better understand N_2O decomposition steps.

Results and discussion.

As part of the results, the concentration of the active site, Fe^{2+}, of the different catalysts was quantified by in situ FTIR, using NO as a probe molecule. We have also discussed the correlation between the amount of Fe^{2+} detected and the activity for N_2O decomposition. By *operando* FTIR we have identified key steps in the mechanism by monitoring structural bands of the solid sensitive to the iron oxidation state. This provided important information on the reaction mechanism, revealing the oxidative role of active oxygen produced by N_2O decomposition, the consecutive formation of HO-Fe species, and the effect of reducing gases addition in the flow to recover the Fe^{2+} active sites. Additionally, we have demonstrated the role of water and its effect on the deactivation of Fe^{2+} sites (also using D_2O), as well as potential solutions to mitigate this effect. Using ^{15}NO and $^{18}O_2$ isotopic gases we have shown the spectator role of molecular O_2 in the chemistry of the decomposition reaction, but also its effect as a physical competitor for adsorption on the catalytic surface.

All in all, the combination of *operando* IR spectroscopy in relevant industrial conditions and the use of isotopic species have permitted us to achieve a complete description of the catalytic decomposition of N_2O on iron-based zeolites and a thorough description of active sites and their evolution during the reaction. This will allow designing a new generation of catalysts with enhanced properties for greenhouse gas elimination.

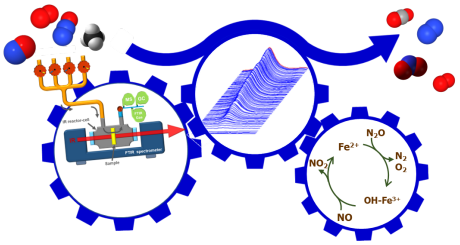

Figure 1: Graphical representation of the mechanism of DeN_2O under relevant industrial conditions

Revealing the Formation and Reactivity of Cage-Confined Cu Pairs in Catalytic NOx Reduction over Cu-SSZ-13 Zeolites by in situ UV-Vis Spectroscopy and Time-Dependent DFT Calculations

Hurong Lei [1,2], Daiqi Ye[2], Peirong Chen[2,*], Ulrich Simon[1]

[1]*Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1a, 52074 Aachen, Germany*
[2]*School of Environment and Energy, South China University of Technology, 510006 Guangzhou, China*
[*] Corresponding Author's E-mail address: *chenpr@scut.edu.cn*

Keywords: Cu redox, in situ DRUVS, in situ DRIFTS, TD-DFT calculation, cage-confined Cu pair

Introduction. The low-temperature mechanism of chabazite-type small-pore Cu-SSZ-13 zeolite remains a debate and needs to be clarified for further improvement of NH_3-SCR performance. It is a consensus that the redox cycle of $Cu^{II} \leftrightarrow Cu^{I}$ dominates the overall activity of low-temperature SCR, involving the essential $[Cu^{II}_2(NH_3)_4O_2]^{2+}$ complexes formation generated by two mobile $Cu^{I}(NH_3)_2$ and O_2.[1, 2] Nonetheless, it is still not clear how the two Cu-complex intermediates are interconverted and whether there is any transient, less stable state during the interconversion.

Results and discussion. In this study, we established experimental protocols to follow the dynamic redox cycling (*i.e.*, $Cu^{II} \leftrightarrow Cu^{I}$) of Cu sites in Cu-SSZ-13 during low-temperature NH_3-SCR catalysis by diffuse reflectance *in situ* ultraviolet-visible spectroscopy (DRUVS) and *in situ* infrared spectroscopy (DRIFTS). Further integrating the *in situ* spectroscopic observations with time-dependent density-functional theory (DFT) calculations allows us to identify two cage-confined transient states, namely the O_2-bridged Cu dimers (*i.e.*, μ-η^2:η^2-peroxodiamino dicopper) and the proximately paired, chemically non-bonded $Cu^{I}(NH_3)_2$ sites, and to confirm the $Cu^{I}(NH_3)_2$ pair as a precursor to the O_2-bridged Cu dimer. Comparative transient experiments reveal a particularly high reactivity of the $Cu^{I}(NH_3)_2$ pairs for the NO-to-N_2 reduction at low temperatures. Our study demonstrates for the first time, to the best of our knowledge, direct experimental evidence for the transient formation and high reactivity of proximately paired Cu sites under zeolite confinement, and provides new insights into the strongly debated low-temperature mechanisms of NH_3-SCR catalysis.

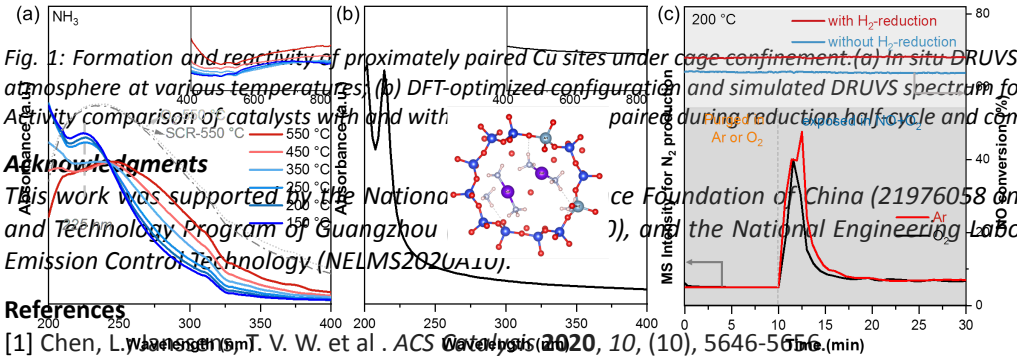

Fig. 1: Formation and reactivity of proximately paired Cu sites under cage confinement.(a) In situ DRUVS spectra of Cu-SSZ-13 in NH_3 atmosphere at various temperatures; (b) DFT-optimized configuration and simulated DRUVS spectrum for the proximately paired; (c) Activity comparison of catalysts with and with paired during reduction half-cycle and complete NH_3-SCR reaction.

Acknowledgments

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Distant Binuclear Vanadium V(II) Cationic Sites in the Ferrierite Zeolite. A DFT study of their properties

Mariia Lemishka[1,2]*, Jiri Dedecek[1], Agnieszka Monika Kornas[1], Edyta Tabor[1], Stepan Sklenak[1]

[1] *J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Prague, Czech Republic*
[2] *Faculty of Chemical Technology, University of Pardubice, Pardubice, Czech Republic*
* *mariia.lemishka@jh-inst.cas.cz*

Keywords: zeolites, vanadium active centers, DFT calculations, *α*–oxygen.

Introduction. The distant binuclear cationic sites were firstly identified using theoretical modeling in the context of the study of the N_2O decomposition over the Fe(II) cation exchanged ferrierite, the beta zeolite, and ZSM–5 (i.e., Fe–ferrierite, Fe–beta, and Fe–ZSM–5, respectively) [1]. We devised that the presence of the active sites formed by the distant binuclear Fe(II) centers explained the exceptional activity of Fe–ferrierite in comparison with the Fe–beta and Fe–ZSM–5 catalysts [2]. The first chemical step of the N_2O decomposition is the formation of the *α*–oxygen species [2,3] [i.e., $(Fe(IV)═O)^{2+}$] which exhibits unique oxidation properties reflected in an outstanding activity in the oxidation of methane to methanol at room temperature [3]. Furthermore, we predicted for the first time employing periodic DFT calculations and subsequently confirmed experimentally that the ferrierite zeolite exchanged with other transition metal cations able of the M(II) to M(IV) redox cycle could be employed for the preparation of the *α*–oxygen species [i.e., $(M(IV)═O)^{2+}$] using N_2O [3].

Moreover, we firstly predicted using the power of periodic DFT calculations that these distant binuclear cationic sites were able to split dioxygen to yield pairs of the distant *α*–oxygen species. Subsequently, experiments were performed at room temperature and the theoretical prediction of a cleavage of dioxygen to give a pair of the distant *α*–oxygen atoms was confirmed experimentally and thus splitting dioxygen was discovered [4].

Methodology. Periodic DFT employing the VASP program.

Results and discussion. In this contribution, we report on our investigation regarding the structure and oxidation properties of the distant binuclear vanadium V(II) cationic sites as an example of the distant binuclear cationic sites formed by early transition metal cations.

Acknowledgments
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Elucidating the effects of promoters on rhodium catalysts in the CO_2 hydrogenation to alcohols using DRIFTS

R. van der Pluijm, A. Bansode*, A. Urakawa*

Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands, * *a.b.bansode@tudelft.nl, a.urakawa@tudelft.nl*

Keywords: Heterogeneous catalysis, CO_2 hydrogenation, *in situ* DRIFTS, Mechanistic study, Ethanol

Introduction Climate change caused by increasing carbon emissions is one of today's greatest challenges. This challenge has sparked global interests in finding renewable, more sustainable fuels. One possibility is to combine emitted CO_2 with green hydrogen to synthesize fuels, closing the carbon cycle. It has been known for a couple of decades that certain promoted rhodium (Rh) catalysts can catalyze the CO_2 hydrogenation reaction to ethanol (EtOH).[1] However, still little is known about the reaction mechanism and the role of the promoters.[2] In this work transient *operando* DRIFTS studies in combination with multivariate curve resolution (MCR) analysis is used to gain more insight into the reaction mechanism and to understand exactly why the addition of Fe and Li promoters enhances the ethanol selectivity.

Experimental/methodology All the catalysts were prepared via impregnation method. Transient *in situ* DRIFTS experiments were performed using a Thermo Scientific Nicolet 6700 FT-IR spectrometer and a custom DRIFTS cell with a ZnSe window at a pressure of 20 bar. A four-way switching valve was used to apply perturbations to the system (e.g. switching between CO_2 and H_2 in 15-minute intervals). The product stream was continuously analyzed using a mass spectrometer.

Results and discussion It was found that the addition of promoters (Fe, Li) introduces formate on the catalyst surface, which might provide an additional carbon source for ethanol production. Additionally, it was found, during the CO_2-H_2 switching experiment (Fig. 1), that EtOH and CH_4 are formed during the CO_2 phase, while MeOH is formed during the H_2 phase. It was postulated that the promoters induce the presence of oxidized rhodium on which linear carbonyl species can bind. This linear carbonyl on oxidized rhodium might be more active in forming the acetyl species than linear carbonyls. This acetyl species could then be further hydrogenated to ethanol.

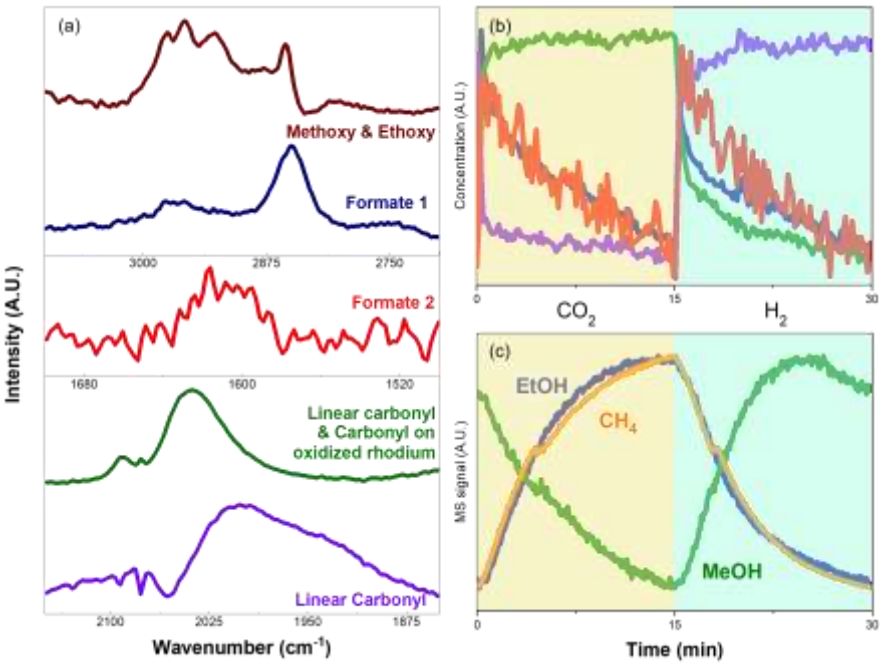

Figure 1 Reactant switching experiment on 1wt% $RhLi/SiO_2$, for 15 minutes a flow of 20 mL/min CO_2/He with a ratio of 1/3 is ran across the catalyst, after this for 15 minutes a flow of 20 mL/min H_2/He with a ratio of 3/1 is ran across the catalyst at 180 °C and 20 bar. (a) MCR resolved spectra of the obtained DRIFTS results (b) MCR resolved concentration profiles of the MCR resolved spectra, the concentration profiles correspond to their respective spectra with the same colors (c) normalized response of EtOH, CH_4 and MeOH measured by MS in the outlet gas.

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Hierarchical Pore Networks: Comparison Between Differential Cycling High-Resolution Mercury Porosimetry, Classical Mercury Porosimetry, and Reverberi Technique

Luca Lucarelli[1]*, Anthony W. Thornton[2], and Jeffrey C. Kenvin[2]

[1]*Micromeritics Srl, Via Montegna 21, 22096 Pioltello (Milano) Italy*
[2]*Micromeritics, 4356 Communications Drive, Norcross, GA 30093- USA*
**luca.lucarelli@micromeritics.com (corresponding author)*

Keywords: mercury porosimetry, pore size, throat size, cavity volume, catalyst support, pore networks, hierarchical porosity

Introduction. The void structure of porous materials used as catalyst supports affects several properties such as permeability to liquids, gas diffusion, access of organic molecules, availability of oxidation/reduction active sites, etc. Mercury intrusion porosimetry has been widely used to investigate the accessible pore volume starting from about 3.6 nm up to more than 600 µm. The main limitation of mercury porosimetry is related to the measure of the access size to the porous network, to which the volume of mercury intruded, thus the pore volume, is associated. This generates an image of a simple bundle of cylindrical capillaries that might jeopardize further calculations that are related to pore size and pore volume, like permeability and diffusion. An advanced technique of differential cycling porosimetry [1] has been applied to several catalyst supports to better describe the porous network distinguishing the access channels' volume and size (pore throats) from the internal junction void volumes (pore cavities).

Experimental/methodology. Eight commercially available alumina catalyst supports were analyzed using repeated mercury intrusion cycles. Catalyst supports have been first measured by a classic intrusion/ extrusion mercury porosimetry up to about 400 MPa. The obtained curve is then used to evaluate the required pressure steps to better define the intrusion pressure region. Once the cycling steps are defined, fresh samples are submitted to pressurization up to the first step followed by a depressurization back to about atmospheric pressure, measuring at this point the residual volume of mercury trapped in the cavity. The porosimeter then is going to the next pressure step, as stated by the preliminary evaluation, to go back again to atmospheric. Cycles are repeated up to the maximum pressure of over 400 MPa. The distinction between the pore throats and pore cavity volumes is attainable by subtracting the residual mercury volume from the total intruded volume for each cycle.

Results and discussion. The differential cycling porosimetry technique provides additional information on materials with a complex pore structure distinguishing the access volume and size from the cavity volumes. Cavity volumes can then be put in relation to the average access size determined by the intrusion pressures. The method might help to better investigate different catalyst behaviors, despite having similar physical and chemical properties, when diffusion or permeation phenomena are affecting the catalyst efficiency or selectivity. A detailed comparison of cycling porosimetry with more classical mercury porosimetry methods and the Reverberi technique [2] is described in the present work.

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The Role of Surface Species on Platinum in Selective Ammonia Oxidation to Nitrogen

Vasyl Marchuk[1], Dmitry I. Sharapa[2], Felix Studt[1,2], Jan-Dierk Grunwaldt[1,2], and Dmitry E. Doronkin[1,2*]

[1]*Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology, Engesserstr. 20, 76131 Karlsruhe, Germany.*
[2]*Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.*
[*]*E-mail: dmitry.doronkin@kit.edu*

Introduction. Ammonia is regarded as a promising alternative to hydrogen for renewable energy storage [1]. Ammonia has high energy density and can be easily liquified and transported through the existing well-established infrastructure to a place of energy demand. However, technologies for recovering energy from ammonia, such as combustion or cracking to hydrogen for fuel cells, suffer from incomplete conversion. To remove the residual ammonia, ammonia slip catalysts (ASCs) need to be applied. They are typically based on supported Pt and are used to selectively oxidise ammonia to nitrogen and water. To improve the activity and selectivity of ASCs, it is important to unravel the surface species on Pt participating in the reaction mechanism and their effect on catalytic performance. Most of the studies on the reaction intermediates probe them under vacuum or on unsupported Pt [2,3]. Such model conditions do not allow to account for the role of support and all the moieties present under atmospheric pressure (e.g. N_2O or bulk oxides) [2,4]. Hence, this study focuses on identifying species participating in ammonia oxidation on supported Pt under atmospheric pressure which can be achieved by using *operando* X-ray absorption spectroscopy (XAS) [5].

Experimental. *Operando* XAS was used to detect spectral trends reflecting the reaction mechanism on Pt/Al_2O_3 catalysts. Further, the species at the origin of these spectral trends were identified with kinetic studies, *operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), *in situ* XAS in the atmospheres of reaction products/educts. Additionally, the geometries of Pt containing possible reaction intermediates on the surface were optimised with density functional theory (DFT) and used to calculate their Pt L_3 edge XAS spectra and to compare them with experimental spectra.

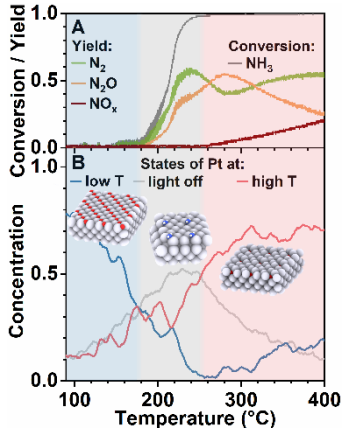

Figure 1. Species in top layers of Pt governing its catalytic performance.

Results and discussion. Three main states of Pt surface were identified during light offs in reaction mixture. Their evolution correlated with catalytic activity and selectivity (see fig. 1). The first state was predominant at low temperatures. It corresponded to inactive Pt poisoned by O. The second state prevailed at light off temperatures. It was attributed to more reduced Pt surface covered with

NH_3 and its dissociation products. This state related to high activity and selectivity to N_2. The third state evolved as Pt surface started lacking ammonia due to its high conversion at elevated temperatures. Under these conditions oxygen probably diffuses into the subsurface of Pt. This state did not decrease catalytic activity but could be associated with low selectivity.

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Identification of the active centres in FER and MOR for N_2O processing

M.C. Campa[1], D. Pietrogiacomi[2], C. Catracchia[2], J.E. Olszowka[3], K. Mlekodaj[3], M. Lemishka[3,4], J. Dedecek[3], E. Tabor[3*]

[1]*CNR-ISMN, c/o Chemistry Department, Sapienza University of Rome, Rome, Italy*

[2]*Chemistry Department, Sapienza University of Rome, Rome, Italy*

[3]*J. Heyrovský Institute of Physical Chemistry of the CAS v. v. i. Prague, Czech*

[4]*Faculty of Chemical Technology, University of Pardubice, Pardubice, Czech Republic*

[*]*E-mail: edyta.tabor@jh-inst.cas.*

Keywords: zeolites, iron active centers, Al distribution, N_2O abatement.

Introduction. Elimination of greenhouse gases N_2O originating from the production of chemicals (adipic acid and nitric acid plants), the fossil-fuel combustion processes (power plants), and the three-way catalytic converters (TWCs) represent one of the goals of environmental catalysis [1-3]. Iron zeolites are known as effective catalysts for the N_2O abatement process in the presence of NOx. [1]. In this study, we focused on the analysis of the influence of zeolite structure and population of iron active sites controlled by Al atoms organization on the N_2O abatement reactions.

Experimental/methodology. Two Fe-MOR and two Fe-FER with similar Fe wt.% ~1 and ~2 were selected as model catalysts for N_2O abatement via decomposition in the absence or presence of NO ($DecN_2O$ or $DecN_2O$+NO), or via reduction with CH_4 in the absence or presence of excess O_2 (CRN_2O or $SCRN_2O$). The methododlogy of catalytic tests included in-situ UV-Vis, and in-situ opernado FTIR studies.

Results and discussion. Catalytic results showed that Fe-FER catalysts were markedly more active than Fe-MOR at similar Fe-loading for the $DecN_2O$ and $DecN_2O$+NO, and slightly more active for the $SCRN_2O$, whereas for the CRN_2O they showed similar activity. This suggests the influence of the reactant mixture on the iron oxidation state during the catalytic cycle. In situ UV–vis DRS experiments performed over Fe-MOR and Fe-FER, in which samples were oxidized by N_2O at 250 °C and reduced by CH_4 at 250 °C, showed different mobility of the redox couple Fe^{3+}/Fe^{2+} in the presence of the various reactants in MOR and in FER, which is in agreement with catalytic results. Operando-FTIR experiments on Fe-FER showed (i) the activation of N_2O assisted by Fe-OH species (formation of an intense OH signal at 3644 cm^{-1}) in N_2O flow, and (ii) the activation of CH_4 via oxidative dehydrogenation (formation of Fe^{2+}-CO) in CH_4 flow. Methoxy/formaldehyde/formate species formed in N_2O+CH_4 flow in both Fe-MOR and Fe-FER, that possessed a similar reactivity. After O_2 addition to the mixture, in Fe-FER methoxy/formaldehyde/formate species were stable, whereas in Fe-MOR specific formate species decreased while the activity decreased.

All results suggest that N_2O reduction with CH_4 required Fe^{2+}-containing bifunctional active sites. In the presence of O_2 all these sites are stable in FER, whereas a fraction of them is oxidized in MOR. The cation siting affecting iron reactivity toward N_2O abatement is discussed.

Acknowledgments

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SO_2 poisoning of the Cu-CHA deNO_x catalyst monitored by X-ray absorption spectroscopy

A.Yu. Molokova[1,2], G. Berlier[2], E. Borfecchia[2], T.V.W. Janssens[3], S. Bordiga[2], F. Wen[4], P.N.R. Vennestrøm[3], K.A. Lomachenko[1]

[1] *European Synchrotron Radiation Facility, 71 avenue des Martyrs, 38043 Grenoble, France*

[2] *Department of Chemistry and NIS Centre, University of Turin, via Giuria 7,10125 Turin, Italy*

[3] *Umicore Denmark ApS, Kogle Allé 1, 2970 Hørsholm, Denmark*

[4] *Umicore AG & Co, Rodenbacher Chaussee 4, 63457 Hanau, Germany*

[*] *molokova@esrf.fr*

Introduction. The emission of nitrogen oxides (NO_x) from diesel vehicles is a major contributor to air pollution around the world. Cu-exchanged chabazite zeolites (Cu-CHA) are efficient and stable catalysts for the abatement of these NO_x emissions via the selective catalytic reduction of NO by NH_3 to N_2 and H_2O (NH_3-SCR). However, the application of Cu-CHA catalysts for NH_3-SCR is limited, because the presence of SO_2 can cause significant deactivation of Cu-CHA catalysts below 300 °C [1-3]. The interaction of SO_2 with Cu-CHA catalysts depends on the state of the Cu [4]. To obtain further insight in the SO_2 deactivation mechanism of the Cu-CHA catalysts for NH_3-SCR we identify the Cu-species that react with SO_2 using in-situ X-ray absorption spectroscopy (XAS), by carefully preparing well-defined Cu-species and expose these to SO_2 at 200 °C.

Experimental The XAS measurements were done at the BM23 beamline of the ESRF (European Synchrotron Radiation Facility). A Cu-CHA catalyst (Si/Al=6.7, 3.2 wt% Cu) was pre-treated in six different ways, to form well-defined Cu^{I} or Cu^{II} species with and without NH_3. The reactivity of these Cu species with SO_2 was monitored by the changes in the XAS spectra during exposure to 400 ppm SO_2 at 200 °C. The effect of O_2 on this reactivity was determined by exposing the different Cu species to a mixture of 100 ppm SO_2 and 10% O_2. Furthermore, the SO_2-uptake was determined by X-ray adsorbate quantification (XAQ) [5] and temperature programmed desorption of SO_2.

Results and discussion. While the XAS spectra of the Cu^{I} species and Cu^{II} species in absence of NH_3 remain largely unaffected by the SO_2 at 200 °C, the XAS spectra of the $[Cu^{II}(NH_3)_4O_2]^{2+}$ and Cu^{II}+NH_3-states change significantly, indicating that SO_2 reacts with Cu^{II} in the presence of NH_3. In these cases, the characteristic pre-edge peak at 8983 eV for the $Cu^{I}(NH_3)_2$ complex [6] becomes more pronounced, indicating that the exposure to SO_2 leads to some formation of Cu^{I}. With the mixture of O_2 and SO_2, no Cu^{I} is observed, but the local geometry changes upon the interaction with SO_2. SO_2-TPD on the SO_2 exposed samples and XAQ results during the exposure to SO_2 also showed the largest uptake of SO_2 by $[Cu^{II}(NH_3)_4O_2]^{2+}$ and Cu^{II}+NH_3-states, corroborating these results, and the presence of O_2 leads to a larger uptake of SO_2. Because the $[Cu^{II}(NH_3)_4O_2]^{2+}$ complex is a key intermediate in the NH_3-SCR reaction cycle, the poisoning of the Cu-CHA catalyst by SO_2 seems to be a chemical poisoning caused by the strong interaction of this $[Cu^{II}(NH_3)_4O_2]^{2+}$ comples with SO_2, which is further enhanced by O_2.

Acknowledgments

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Restructuring of TiO_x Overlayers over Ni Nanoparticles during Catalysis

Matteo Monai[1], Kellie Jenkinson[2], Angela E. M. Melcherts[1], Jaap N. Louwen[1], Ece A. Irmak[2], Sandra Van Aert[2], Thomas Altantzis[3], Charlotte Vogt[1], Ward van der Stam[1], Tomáš Duchoň[4], Břetislav Šmíd[5], Esther Groeneveld[6], Peter Berben[6], Sara Bals[2,*] and Bert M. Weckhuysen[1,*]

[1] *Inorganic Chemistry and Catalysis group, Utrecht University, Utrecht (The Netherlands).*

[2] *EMAT and NANOlab Center of Excellence, University of Antwerp, Antwerp (Belgium).*

[3] *ELCAT, University of Antwerp, Wilrijk, (Belgium).*

[4] *Peter-Grünberg-Institut 6, Forschungszentrum Jülich GmbH, Jülich (Germany).*

[5] *Department of Surface and Plasma Science, Charles University, Prague (Czech Republic).*

[6] *BASF Nederland B.V., Strijkviertel 61, De Meern (The Netherlands).*

*sara.bals@uantwerpen.be, b.m.weckhuysen@uu.nl

Introduction. Supported metal catalysts are known to respond to pretreatment and reaction conditions by restructuring [1]. An example of catalyst restructuring is the embedding of metal nanoparticles (NPs) by overlayers of reducible supports, such as TiO_2, following high temperature reduction [2]. Here, we show that TiO_x overlayers formed on Ni/TiO_2 catalysts are completely removed or partially restructured under CO_2 hydrogenation conditions, depending on the reduction temperature.

Experimental/methodology. 6 wt.% Ni/ TiO_2 P25 catalysts were prepared by deposition precipitation, and studied by *operando* TEM (H_2 or 1:3 CO_2:H_2, 1 bar, 400–600°C), on an aberration-corrected ThermoFisher Scientific Titan Cubed EM, in a climate G+ nanoreactor (DENS solutions). *Operando* FT-IR spectroscopy was performed on a Bruker Tensor 37 spectrometer, in a HTHP Specac cell (CO_2:CO:H_2 mixtures, 200–400 °C).

Results and discussion. The Ni/TiO_2 catalysts were reduced at 400 or 600 °C to induce different degrees of overlayer formation. After 400 °C reduction, a TiO_x overlayer formed selectively over Ni (111) facets, which was completely removed upon exposure to CO_2 hydrogenation conditions, leading to NPs restructuring (Figure 1A-D). After 600 °C reduction, a complete encapsulation by TiO_x was shown by both *operando* TEM and H_2 chemisorption. Such layer was only partially removed under CO_2 hydrogenation conditions, forming a patchy TiO_x overlayer, and exposing about half of the Ni sites to the gas atmosphere (Figure 1E,F). This led to the formation of Ni interfacial sites in contact with TiO_x and resulted in higher TOFs for CO_2 methanation and C–C coupling for the 600 °C-reduced catalyst. We propose that the increased Ni–TiO_x interface aided C–C coupling by providing a reservoir of carbon species in close contact with adsorbates on Ni.

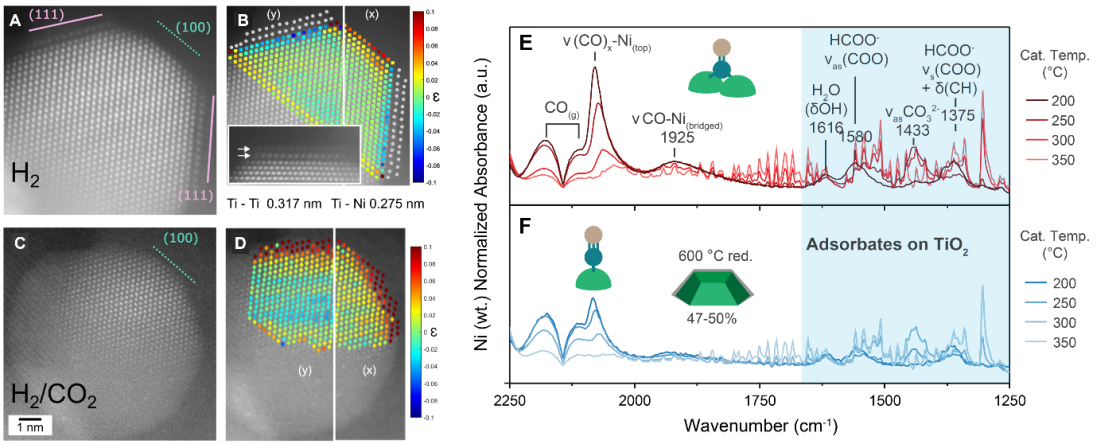

Figure 1. (A) A representative atomic resolution HAADF-STEM image of a Ni nanoparticle (NP) in a Ni/TiO_2 catalyst (H_2, 400 °C). Solid lines indicate TiO_x-covered Ni atomic planes and dashed lines indicate bare facets. (B) Estimated positions of Ti (gray) and Ni atomic columns (color scale for strain). (B insert) Close-up of the TiO_x bilayer, where white arrows highlight each Ti layer. (C) HAADF-STEM image of the same particle as in (A) upon exposure to a CO_2:H_2 (0.25: 0.75 bar, 400 °C) showing complete re-exposure of Ni and NP restructuring. (D) Estimated atomic columns positions of Ni from the particle shown in (C). (E,F) *Operando* FT-IR spectra under CO–CO_2 hydrogenation conditions over Ni/TiO_2 reduced at (E) 400°C and (F) 600°C, with the estimate of Ni coverage (47-50 %) at 300 °C.

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Identifying the species producing ethylene and propylene in the methanol-to-olefin reaction by *operando* spectroscopy

J. C. Navarro, S. Chung, T. Li, J. Ruiz-Martínez*

King Abdullah University of Science and Technology, KAUST Catalysis Center (KCC), Thuwal 23955-6900, Saudi Arabia

**javier.ruizmartinez@kaust.edu.sa*

Keywords: Methanol to olefins, UV-Vis spectroscopy, reaction mechanism.

Introduction

Global demand of olefins is based on fossil fuel sources, but they are limited, so the search for new alternatives is required. One of these alternatives is methanol, which can be converted into polymer-grade alkenes over acidic zeolites. Such processes are known as the methanol-to-olefin (MTO) reaction. Although the MTO process is already commercialized, the mechanism of methanol conversion is complex, and it has still not been thoroughly understood. More specifically, the active species governing the selectivity towards ethylene and propylene are not well understood yet [1].

Results and discussion

Considering the aspects mentioned, the present work is focused on understanding the species controlling olefin selectivity via *operando* UV-Vis spectroscopy. For that purpose, we have chosen H-Beta as model zeolite as we found that the propylene/ethylene ratios can be easily modified by changing the SiO_2/Al_2O_3 ratio (SAR). Six Beta samples with SAR = 25, 38, 75, 100, 150, and 300 (Zeolyst International) were used. Interestingly, propylene/ethylene ratios are increased when the SAR increased, to a level where such ratio is over 60 with the samples with SAR 300 (**Fig. 1a**). Looking at the UV-Vis spectra for the tested zeolites under operando conditions (**Fig. 1b**), we noticed that the band ascribed to alkylated benzene carbocations with low degree of alkylation (≈342 nm) decreases with respect to the band attributed to monoenyl/cyclopentenyl carbocationic species (≈286-299 nm) when SAR increases. A clear correlation was obtained when plotting the ratio of the intensity bands with the propylene/ethylene ratio (**Fig. 1c**), which suggest that low alkylated benzene species are predominantly ethylene makers and monoenyl/cyclopentenyl species are in charge of the production of propylene [2]. A similar trend was also observed in H-ZSM-5 samples.

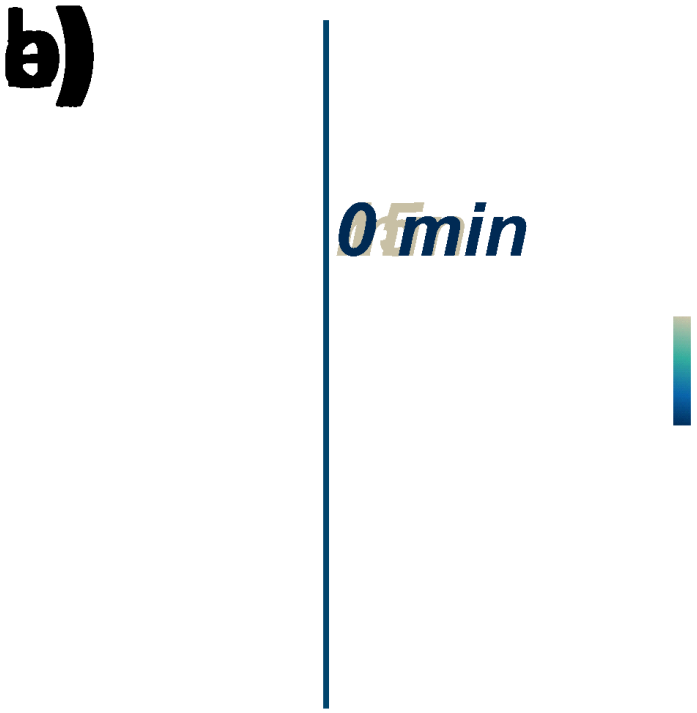

Figure 1. a) Catalytic performance for BEA zeolites with different SAR (400°C, 1 atm, WHSV = 4 h^{-1}), **b)** UV-Vis spectra for BEA (SAR=25, 150 and 300), and **c)** Bands correlation versus $C_3^=/C_2^=$ ratio for BEA (SAR= 25, 150 and 300)

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Kinetic and operando UV-vis study of NH_3-SCR over V/TiO_2

A. Lanza[1,2], R. Resmini[1], J. Gopakumar[3], D. Chen[3], K. Rut[3], C. Negri[1], M. Maestri[1], A. Beretta[1*]

[1]*Politecnico di Milano, Milan, Italy;* [2]*Johnson Matthey Technology Centre, Sonning Common, United Kingdon*

[3]*NTNU, Trondheim, Norway ,* [*]*alessandra.beretta@polimi.it*

Keywords: NH_3-SCR, Operando UV-vis, redox kinetics, HCl promotion, modelling analysis

Introduction. NH_3-SCR over V-catalysts is known to involve V redox cycle. In [1] dynamic testing and operando FTIR showed a remarkable promoting effect of V-doping with HCl, which was associated to a selective enhancement of NO oxidative activation; this, in turn, supported the identification of V reduction as rate determining step of the process. In this work, operando UV-vis experiments were performed to further investigate the redox kinetics; conversion and d-d transition measurements were acquired simultaneously and their quantitative analysis was based on reactor and kinetic modelling tools, looking for an insight of the dependence of site distribution on operating conditions and HCl addition.

Experimental. A 2%V/TiO_2 was tested in a operando UV-Vis rig, with a quartz reactor connected to a MS. After preoxidation at 450°C, the catalyst was coold to the desired teperature in the range 150-300°C and the SCR test was performed (NO=NH_3=1000 ppm, O_2=0.25-10%). A series of tests were also run by adding a chlorination treatment (HCl=100 ppm+O_2=10%) prior to the SCR test. The oxidation state of V was monitored by an external UV-vis probe; the fraction of reduced V^{5+} sites was obtained by the d-d transition band at 670 nm (the fingerprint of V^{+4}). The maximum fraction of reducible V^{+5} was determined by the extent of the d-d transition at 400°C in a O_2-free test with NO+NH_3=1000 ppm after preoxidation.

Results and discussion. NH_3-SCR tests were perfomed at varying temperature and O_2 concentration with and without HCl-preadsorption on the catalyst bed. Data were modelled by assuming a 1D plug-flow reactor model and a red-ox rate expression, that combines the single steps of oxidation and reduction; the distribution of reduced and oxidized sites (in terms of σ_{ox} / σ_{red} ratio and coverage of oxidized sites σ_{ox}) could be obtained as function of gas phase composition and intrinsic rate contants, as shown in the Table.

Table – Red-ox rate expression

$r = \left(\frac{\sigma_{ox}}{r_{reduction}} + \frac{\sigma_{red}}{r_{oxidation}}\right)^{-1}$	$r_{reduction} = k_{NO} \cdot P_{NO} \cdot \sigma_{ox} \cdot \theta_{NH_3}$ with θ_{NH_3} θ_{NH_3} =1 under large NH3 conc [2]	$r_{oxidation} = k_{ox} \cdot P_{O_2}^{n} \cdot \sigma_{red}$ with n= ¼ [2]	$\frac{k_{NO} \cdot P_{NO}}{k_{ox} \cdot P_{O_2}^{1/4}} = \frac{\sigma_{ox}}{\sigma_{red}} = \frac{\sigma_{ox}}{1-\sigma_{ox}}$

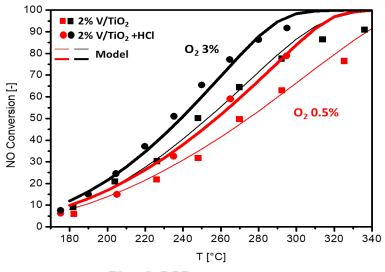

Fig. 1 SCR tests

The rate constants k_{NO} k_{NO} and k_{ox} k_{ox} were estimated from the conversion data with and without HCl doping (Fig. 1). HCl promoted the kinetics and the model analysis confirmed that the rate of reduction grew more importantly than that of oxidation. The model was then applied to predict the site distribution along the reactor, under the conditions explored. The simulated values of σ_{ox} at mid bed length were compared with the d-d transition obtained from UV-vis (Fig. 2), taken as representative of the central zone of the bed. The spectroscopic data showed an increasing trend of σ_{ox} at increasing T, which is in line with the predicted effect of temperature on site distribution due to the local progressive decrease of NO concentration and extinction of the reduction step. At low T, UV-vis showed a larger extent of reduced V sites after HCl-pretreatment, which well agreed with the estimated promotion of HCl on the rate of the reduction step. While the nature of HCl-V-NO interaction is under investigation, this

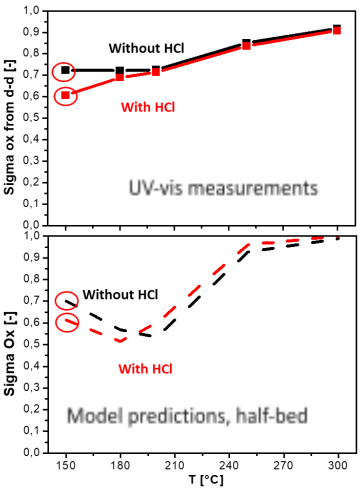

Fig.2 Measured and calculated s_{ox}

work demonstrated the potential of a methodology, where the kinetic analysis supports the interpretation of UV-vis data (as herein addressed) and may guide the design of kinetically relevant operando experiments.

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SiO_2-Supported Co_xPt_y Nanoalloys for the Dry Reforming of Methane

D. Niedbalka[1], L. Thommen[1], P. M. Abdala[1*], C. R. Müller[1*]

[1]*Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zurich, Switzerland*
*abdalap@ethz.ch, *muelchri@ethz.ch*

Keywords: strong electrostatic adsorption, alloys, cobalt, platinum, nanoparticles

Introduction. The dry reforming of methane (DRM) allows converting two major greenhouse gases, CH_4 and CO_2, to produce H_2 and CO (syngas). This reaction is catalyzed by noble or transition metals supported on metal oxide supports and requires high temperatures (600 – 1000 °C) to achieve high conversions. However, many catalysts for DRM suffer from deactivation due to carbon deposition, particle growth, and oxidation. Bimetallic nanoparticles offer a versatile strategy to overcome the limitations of monometallic systems via the tuning of the catalysts' electronic and/or geometric structure.[1] Here, we report the development of SiO_2-supported Co_xPt_y model catalysts aiming to understand the effect of the ratio of Co : (Co+Pt) on the catalyst's structure and catalytic performance.

Experimental/methodology. Mono- and bimetallic Co_xPt_y/SiO_2 catalysts were synthesized by strong electrostatic adsorption (SEA).[2] The precursors $[Co(NH_3)_6]Cl_3$ and $Pt(NH_3)_4(OH)_2{\cdot}xH_2O$ were dissolved in DI H_2O and the pH was adjusted to 11. The Co to Pt precursor concentrations were varied to obtain the desired Co to Pt ratio. The catalysts were dried in air and pre-reduced at 800°C in 10 % H_2/N_2 for 1 h. The DRM reaction was performed at 800 °C with a space velocity of 75 L g_{cat}^{-1} h^{-1}. The catalysts were characterized by a variety of techniques including X-ray powder diffraction, X-ray absorption spectroscopy, H_2 temperature-programmed reduction and Raman spectroscopy.

Results and discussion. SEA nanoparticles of Co_xPt_y that are highly dispersed on the SiO_2 support were obtained (diameter in the range of 1.7 – 3 nm, Figure 1A). We observe that the catalytic activity (CH_4 and CO_2 conversions) and stability are drastically affected by the ratio Co : (Co+Pt). While Pt/SiO_2 deactivates quickly under DRM conditions, Co/SiO_2 shows low activities and H_2/CO ratios. The bimetallic Co_xPt_y/SiO_2 system increases the stability and/or enhances the CH_4 conversion (Figure 1B). Interestingly, we observed a volcano-type CH_4 conversion behavior (360 min TOS) with respect to the molar ratio Co : (Co+Pt). Thus, our study demonstrates that fine-tuning the composition of the alloy is a versatile design tool to yield active and stable CoPt-based catalysts for DRM. The formation of a Co_xPt_y nanoalloy with a molar ratio Co : (Co+Pt) = 0.45-0.55 showed the best catalytic performance likely due to a combination of geometrical and electronic effects.

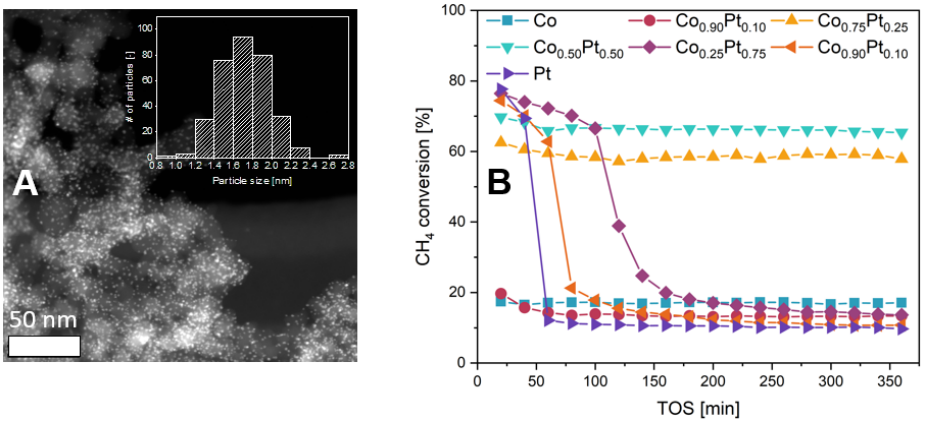

Figure 1: A) STEM image of $Co_{0.50}Pt_{0.50}/SiO_2$ (reduced at 800 °C in 10 % H_2/N_2 for 1 h), $d_{(S)TEM}$ = 1.73 ± 0.23 nm (N = 326). B) CH_4 conversion of the series of Co_xPt_y/SiO_2 catalysts under DRM conditions (75 L g_{cat}^{-1} h^{-1}, 800 °C).

Acknowledgments
Dr. Agnieszka Kierzkowska and Dr. Felix Donat for ICP-OES and (S)TEM images (ScopeM).

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Neutron Reflectometry Reveals the Structure of a High-performing SEI Layer for Lithium-Mediated Nitrogen Reduction to Ammonia

V.A. Niemann[1,2], M. Doucet[3*], N.H. Deissler[4], H. Wang[3], P. Benedek[1,2], J.B. Mygind[4], W.A. Tarpeh[1,2], I. Chorkendorff[4], A.C. Nielander[2*], T.F. Jaramillo[1,2*]

[1]*Stanford University, Stanford, CA, USA*
[2]*SUNCAT Center for Interfaces and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*
[3]*Oak Ridge National Laboratory, Oak Ridge, TN, USA*
[4]*Technical University of Denmark, Lyngby, Denmark*
[*]*doucetm@ornl.gov, anieland@slac.stanford.edu, jaramillo@stanford.edu*

Keywords: lithium-mediated nitrogen reduction, solid-electrolyte interphase, neutron reflectometry

Introduction. Ammonia (NH_3) is a critical component of fertilizer that sustains the human population of 8 billion [1]. The main method to produce NH_3, the Haber-Bosch process, is energy-intensive, centralized, and fossil-fuel powered. An electrochemical method, however, would enable decentralized NH_3 production powered by renewables [2]. The most promising electrochemically-driven method, lithium-mediated nitrogen reduction (Li-N_2R), involves the electroplating of Li from an organic electrolyte, which subsequently reacts with nitrogen and a proton source to form NH_3 [2]. A solid-electrolyte interphase (SEI) layer forms during this process as a result of reduced Li reactivity with the electrolyte and is hypothesized to be critical to dictating system performance [2]. Recent work has demonstrated that using fluorinated salts, e.g., lithium tetrafluoroborate ($LiBF_4$), results in superior performance with respect to the commonly-used lithium perchlorate ($LiClO_4$) [2]. Using *operando* neutron reflectometry, we characterized the structure and composition of the $LiBF_4$ and $LiClO_4$ SEI layers, providing structural insight into improved Li-N_2R performance.

Experimental/methodology. Copper (Cu) working electrodes were prepared via physical vapor deposition on a silicon (Si) substrate. The electrolyte composition was either 1 M $LiClO_4$ or 1 M $LiBF_4$ tetrahydrofuran (THF) with either 1%v/v ethanol or no ethanol added. Applied current was cycled between 0 and -0.3 mA/cm^2 and neutron reflectivity measurements were used to characterize the interface [3]. The observed reflectivity profiles were fit as a function of layer thickness, scattering length density (SLD), and roughness to determine layer structure and composition [3].

Results and discussion. Figure 1a-b shows the reflectivity data and fit, and SLD model, respectively, of an experiment on a Cu WE with 1 M $LiBF_4$ and 1 vol% ethanol in THF. A constant current density of -0.3 mA/cm^2 was cycled for 4 mins, then 12 mins, and then the reflectivity data was collected at the subsequent open circuit potential. The SLD profile in Figure 1b indicates the formation of two layers on the Cu electrode surface. Previous work describes the first layer to be likely Li-rich [3], and for $LiBF_4$, it likely contains LiF species [2]. The second layer is likely a diffuse layer containing organics interfaced with deuterated THF (SLD = 6.2) [3]. As compared to the $LiClO_4$ equivalent experiment, the structure of these layers is more stable, where reflectivity data before and after cycling show fewer changes. These results confirm that $LiBF_4$ forms a more stable SEI structure, enabling improved Li-N_2R performance.

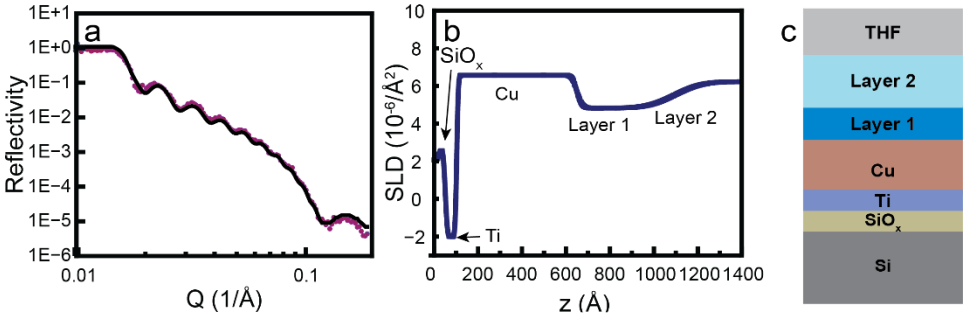

Figure SEQ Figure * ARABIC 1: (a) reflectivity curve after 30 mins constant applied current at -0.3 mA/cm^2 to plate Li using 1 M $LiBF_4$ with 1 vol% ethanol and (b) resulting SLD profile where z = distance from the Si substrate (c) schematic of layers indicated in SLD profile

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An *In Situ* & *Operando* FTIR-DRIFTS-MS Analysis of CDRM Reaction at Low Temperature over Ru-La/ZrO_2 Catalyst

O. Ordulu[1,2], A. Uzun[1,2,3], B. S. Çağlayan[2,3], A. E. Aksoylu[1,2*]

[1]*Department of Chemical Engineering, Boğaziçi University, 34342 Bebek, Istanbul, Turkey*
[2]*SNG&HydTec Lab, Boğaziçi University, 34684 Kandilli, İstanbul, Turkey*
[3]*Advanced Technologies R&D Center, Boğaziçi University, 34342 Bebek, Istanbul, Turkey*
[*]*aksoylu@boun.edu.tr*

Keywords: *Operando* FTIR-DRIFTS-MS, low temperature CDRM, methane, synthesis gas, ruthenium.

Introduction. CDRM is a crucial reaction that converts CH_4 into synthesis gas utilizing CO_2. Two major drawbacks of the reaction are its very strong endothermicity and coke formation. While these acute limitations hinder CDRM to be comfortably utilized, researchers in the last few decades have been studying catalysts which can perform at low CDRM temperatures (T<500 °C). By doing so, coke formation is favored much less and the energy-intensive nature of the reaction is relieved. In this study, a Ru-La/ZrO_2 catalyst was prepared and surface of the catalyst was monitored via FTIR-DRIFTS-MS system in *operando* conditions. The targeted information give insight on the surface mechanism during low T CDRM and the extent of its match with the mechanistic results reported in literature for high T CDRM as well.

Experimental. A 1% Ru-5% La/ZrO_2 catalyst was synthesized by using sequential incipient to wetness impregantion. Reaction temperature was selected as 450 °C for all experiments except room temperature CO adsorption experiments. The study involves characterization experiments with CO at both room temperature and 450 °C, individual CO_2 and CH_4 adsorption experiments, reaction experiments under ideal feed conditions as well as reaction experiments during sequential adsorption of two reactants. All experiments were performed on ZrO_2, La/ZrO_2 and Ru-La/ZrO_2.

Results and discussion. Upon CO adsorption experiments at 450 °C and at room temperature, the most significant differences among DRIFTS spectra of Ru-La/ZrO_2, La/ZrO_2 and ZrO_2 can be seen at carbonyl region. CO failed to adsorb on sole ZrO_2 at any of the two temperatures while it adsorbed on La/ZrO_2 only at 450 °C. On contrary, CO adsorbed on Ru-La/ZrO_2 both at room temperature and at 450 °C. The peak at 1990 cm^{-1} on Ru containing sample is characterized as tricarbonyl species adsorbed on Ru [1] and it is also visible in reaction experiments, confirming the occurrence of CDRM reaction as shown on Figure 1. Simultaneous MS readings made during reaction display presence of water, hence involvement of RWGS reaction (Figure 1, top left). This is expected since RWGS is often reported to be a significant side reaction to CDRM reaction. Results of CO_2 adsorption experiments reveal that addition of La increases interaction of ZrO_2 support with CO_2 which can be traced from elevated intensities of carbonate species (region 1200-1700 cm^{-1}) on spectra of La containing samples compared to observations regarding sole ZrO_2.

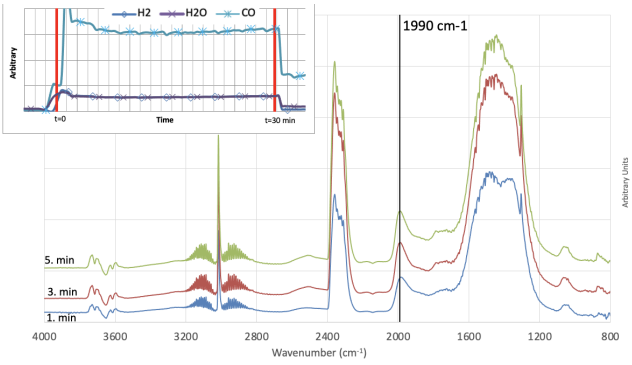

Figure 1: DRIFTS spectra showing transient behavior of Ru-La/ZrO_2 catalyst in reaction conditions with simultaneous MS signals (top left).

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Rigorous Oxidation State Assignments for Supported Ga-Containing Catalysts Using Theory-Informed X-Ray Absorption Spectroscopy Signatures from Well-Defined Ga(I) and Ga(III) Compounds

Fernando D. Vila[1], Jason A. Chalmers[2], Li Li[2], Susannah L. Scott[2], Simon R. Bare[3*]

[1]*Department of Physics, University of Washington, Seattle, WA 98195, USA*
[2]*Department of Chemical Engineering, University of California, Santa Barbara, CA 93106, USA*
[3]*SSRL, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA*
**srbare@slac.stanford.edu*

Introduction. Supported gallium oxides have been widely investigated for their ability to catalyze a variety of energy-related chemical transformations, including the dehydrogenation and dehydroaromatization of light alkanes. In particular, their ability to catalyze the selective dehydrogenation of propane has inspired much interest in the catalysis research community. Under the conditions typically used to achieve these reactions, the Ga species proposed to exist or co-exist include $[GaO_4]^-$, $[Ga_2(OH)_4]$, $[GaO]^+$, $[Ga_2O_2]^{2+}$, $[GaH]^{2+}$, $[GaH_2]^+$, and $[Ga]^+$. Identification of Ga(I) sites in catalysts under reaction conditions relies primarily on X-ray absorption spectroscopy (XAS). However, the observation of a low energy absorption edge is necessary but not sufficient evidence for $[Ga]^+$. There are significant variations in edge position for the XANES of Ga(III) compounds.[1-2] We develop a rigorous set of criteria for characterizing the white line behavior, derived from the experimentally observed and computed properties of several Ga(I) molecular complexes and Ga^+-β´´-Al_2O_3, together with an investigation of the origin of their distinctive features. We report an analysis of the XAS of Ga/HZSM-5 and Ga/γ-Al_2O_3, both of which exhibit low edge energy peaks.

Experimental. XAS spectra at the Ga K-edge (10,367.0 eV), both traditional and HERFD-XANES, were recorded at the Stanford Synchrotron Radiation Lightsource. Theoretical XANES calculations were performed with StoBe 2011 using the PBE exchange-correlation functional.

Results and discussion. To lay a rigorous foundation for characterizing these types of systems and to establish experimental signatures for the elusive Ga(I) oxidation state, Ga K-edge XAS (including HERFD-XANES) were recorded for several well-defined molecular and crystalline Ga(I) compounds. The XANES is essential to establishing the presence of Ga(I), despite the overlap in edge energies with organoGa(III) compounds, because Ga(I)-containing oxide materials show very weak EXAFS scattering. Compared to the XANES of trigonal Ga(III)-containing materials, Ga(I) spectra display a significantly more intense white line feature. Theoretical simulations agree well with this experimental observation, and reveal that the strong XANES intensity originates from the superposition of transitions to several empty, nearly degenerate *p*-like states. These signatures provide compelling evidence for assigning the intense white line in Ga/HZSM-5 and dramatic loss of EXAFS intensity to the near-quantitative reduction of Ga(III) to Ga(I), while the weaker white line and conventional EXAFS signal of Ga/γ-Al_2O_3 point to, at most, a minor fraction of Ga(I) sites. This study provides guidelines to ensure that Ga K-edge XAS data of catalysts are interpreted properly.

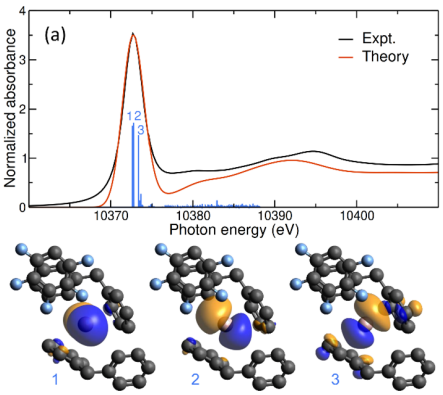

Figure SEQ Figure * ARABIC 1. Comparison of experimental (black) and simulated (red) XANES for [Ga(Ph$_2$CH)$_2$][B(C$_6$F$_5$)$_4$]. The atomically *p*-like molecular orbitals involved in the main transitions that compose the main peak are shown in the computed structures below the spectrum.

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Copper-nickel deoxygenation catalysts
Part II: Adsorption properties determined by TPD

K. Pacultová[1], K. Karásková[1], D. Fridrichová[1], T. Bílková[1], J. Aubrecht[2], B. Shumeiko[2], D. Kubička[2]

[1]*Institute of Environmental Technology, CEET, VSB-Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava, Czech Republic*
[2]*Department of Petroleum Technology and Alternative Fuels, University of Chemistry and Technology Prague, Technická 5, Prague 166 28, Czech Republic*

Keywords: copper-nickel catalysts, anisole, ammonia, TPD

Introduction. Catalytic hydrogenation/deoxygenation can be used for selective transformation of biomass-derived feedstocks into sustainable chemicals or biofuels. To understand this catalytic process, it is necessary to understand the catalyst surface properties - acidity and adsorption/desorption behavior of the catalyst with regard to the organic reactant (anisole).

Experimental/methodology. Ni/Al_2O_3, Cu/Al_2O_3 and bimetallic $Ni\text{-}Cu/Al_2O_3$ catalysts varying in Cu and Ni content were prepared using wet impregnation. For catalyst characterization, TPD of anisole and TPD of NH_3 was used.

Results and discussion. Anisole weakly adsorbed (desorption maxima around 90 °C) on the catalyst surface is adsorbed on the acid sites of the alumina support. The total amount of acid sites decreased with the increasing metal loading, but only in case the metal amount is higher than 5 wt. %. Contradictory to that, the catalyst specific surface area decreased with the increasing metal content only up to 5 wt.% loading. Nickel species in contrast to copper sites have ability to decompose ammonia adsorbed on its surface into hydrogen and nitrogen during TPD NH_3 measurement.

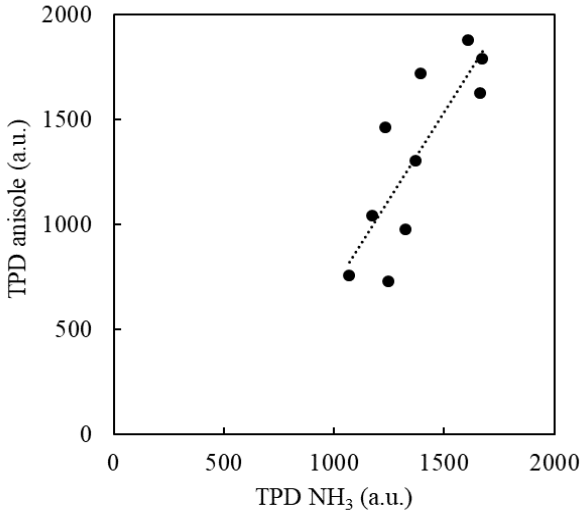

Fig. 1: Dependence of the amount of adsorbed anisole (TPD anisole) on the amount of acid sites (TPD NH_3).

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Effect of Co addition to Pd-CeO_2 for lean methane combustion

L. Pascua-Solé[1], I. J. Villar-Garcia[2], V. Pérez-Dieste[2], C. Escudero[2], N. J. Divins[1*], J. Llorca[1*]
[1]*Institute of Energy Technologies and Department of Chemical Engineering, Universitat Politècnica de Catalunya (EEBE), Avinguda Eduard Maristany 16, 08019, Sant Adrià del Besòs, Barcelona, Spain*
[2]*ALBA Synchrotron Light Source, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallès, Barcelona, Spain*
[*]*corresponding e-mail*: *nuria.jimenez.divins@upc.edu, jordi.llorca@upc.edu*

Keywords: methane combustion, ceria, palladium-cobalt, bimetallics.

Introduction. There has been an increase in natural-gas-fueled vehicles (NGVs) due to the fact that they represent a cleaner option when compared with other fossil fuels [1]. However, methane is a much more powerful greenhouse gas than CO_2, thus it is essential to treat their exhaust gases [2]. Recently, it has been reported that Pd-CeO_2 catalysts prepared by mechanochemical synthesis show outstanding activity for methane combustion [3]. On the other hand, it has been reported on conventionally-prepared catalysts that adding Co to Pd helps them to become more water-resistant [4, 5].

Experimental/methodology. A set of 1 wt.% Pd and 12 wt.% Co mono- and bimetallic samples were prepared by ball milling (BM) and incipient wetness impregnation (IWI). In order to test the activity temperature-programmed combustion (TPC) cycles were performed: 2 cycles from ambient temperature to 900 °C under lean methane conditions and GHSV of 180,000 h^{-1} (0.5% CH_4, 2% O_2, balanced with N_2) followed by a TPC cycle where 10% $H_2O_{(vap)}$ was added. Samples were characterized by *in situ* XAS, XRD and NAP-XPS at ALBA synchrotron. XAS and XRD were acquired on samples subjected to TPC. AP-XPS was performed at 450 °C at 1 mbar pressure with and without the addition of water (1 mL·min^{-1} CH_4, 4 mL·min^{-1} O_2, 2.5 mL·min^{-1} H_2O balanced with N_2).

Results and discussion. The synthesis method does significantly affect the activity of the PdCo system, as represented in Figure 1 (a) by the temperature at which each sample reaches 50% methane conversion. The catalyst prepared by mechanochemical milling is more active than that prepared by IWI. It is accepted that the active phase for methane combustion in Pd-based catalysts is PdO [3]; thus, an increase in the temperature at which the transition of PdO to metallic Pd occurs is desired. From XAS experiments (Figure 1 (b)) it can be seen that the bimetallic sample does not fully convert PdO into metallic Pd, showing the benefits of the addition of Co. Indeed, under reaction conditions Co_3O_4 gets reduced and evolves into CoO. It is worth mentioning that this CoO species is amorphously formed since no peaks of CoO are detected by *in situ* XRD. Similarly, the surface (NAP-XPS) follows a similar behaviour, where PdO does not change into metallic Pd, but Co gets reduced, from Co_3O_4 to CoO.

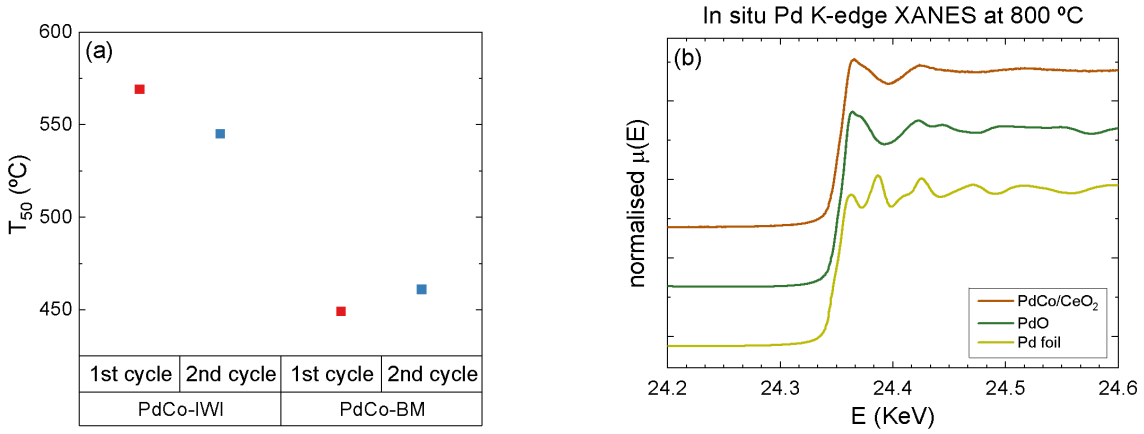

Figure 1. (a) T_{50} of PdCo-BM and PdCo-IWI of the 2 first cycles, without adding water. (b) In situ Pd K-edge XANES spectra of reference samples and PdCo-BM at 800 °C under methane combustion reaction.

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Support effects on ammonia decomposition on supported Cu catalysts

Stefan Peters, Anna Kavaklioti, Sebastian Wohlrab, Ali M. Abdel-Mageed*

Leibniz-Institut für Katalyse (LIKAT), Rostock, Germany
*ali.abdelmageed@catalysis.de

Introduction: The synthesis and non-oxidative decomposition of NH_3 (NOD-NH_3) constitute an efficient cycle for the chemical storage and subsequent release of green H_2. This approach is motivated by the high gravimetric and volumetric H_2 storage capacity of NH_3, which is additionally an easily storable and transportable liquid at room temperature when lightly compressed [1]. On top of that, the well-established chemical production of NH_3 via Haber-Bosch process would accelerate its immediate introduction into the energy infrastructure [2]. Ru-based catalysts are so far the most efficient reported catalysts for the NOD-NH_3 [3]. Cu-based catalysts are promising cost efficient candidates for this reaction, although they do not yet meet the requirements for industrial use [4]. In this work we have systematically investigated the modulation of the electronic and structural properties of Cu nanoparticles, and thus their impact on the catalytic activity for NOD-NH_3. This is achieved by controlled variation of Cu loading (i.e., Cu particle size) and support material, whose interplay affects the metal-support interaction and thus activity for NOD-NH_3.

Experimental/methodology: Catalysts were prepared by wet impregnation of HZSM-5, γ-Al_2O_3 and *m*-ZrO_2 supports with aqueous $Cu(NO_3)_2{\cdot}3H_2O$ at 25°C. After the impregnation step, the catalysts were dried and calcined in air at 400 °C for 4 h. Prior to reaction, catalysts were reduced at 600 °C in 5 % H_2/Ar for 1 h. Kinetic measurements were done in a quartz tube reactor between 300 and 600 °C using an online FTIR gas cell for continuous quantification of NH_3. Catalysts were characterized using *operando* X-ray absorption spectroscopy at Cu K-edge (SOLEIL Synchrotron, *SAMBA* beamline) under conditions identical to that employed in kinetic studies. All samples were additionally characterized before / after reaction using XPS, PXRD, high-resolution STEM/EDS, nitrogen adsorption, and TPX analyses.

Results and discussion: Catalytic decomposition of NH_3 over Cu loaded on different supports showed superior activity of *m*-ZrO_2 supported Cu compared to catalyst based on inert supports such as γ-Al_2O_3 and HZSM-5 at all temperatures between 450 and 600°C. Under steady state conditions at 600 °C Cu/*m*-ZrO_2 catalysts showed about 2-3 times and at least 8 times higher Cu-mass normalized activity than Cu/γ-Al_2O_3 and Cu/HZSM-5 catalysts, respectively. Other supports such as CeO_2-ZrO_2 or graphite were much less active. Optimal catalyst performance was achieved with Cu loadings of 10-15 wt.% but higher intrinsic activity was observed for lower Cu contents. STEM / EDS mapping revealed high dispersion of Cu species on *m*-ZrO_2 and γ-Al_2O_3 both after calcination and after reaction at 600°C. Comparison of the Cu 2p XP spectra of both catalysts indicated a core-level shift towards higher binding energy for Cu/γ-Al_2O_3 compared to Cu/*m*-ZrO_2. This result was supported by H_2-TPR studies which showed the onset reduction of CuO_x species on *m*-ZrO_2 at ~100 °C compared to ≥140 °C for γ-Al_2O_3 catalysts, depending on Cu loading. Thus more facile reduction of a part of CuO_x species is evident on *m*-ZrO_2, which has been attributed to interaction with oxygen defects before [5]. Primary *operando* Cu K-edge XAS investigations (XANES and EXAFS) under reaction conditions indicated the presence of Cu mainly as metallic clusters, while persisting contribution of oxidic species was also observed (shown by Cu-Cu/Cu-O scattering shells in FT data). This Cu-O interaction may refer to the partial binding of Cu atoms to surface oxo- and hydroxo species. Combined with findings from the O 1s XP spectra it can be concluded that reaction induced oxygen vacancy formation in ZrO_2 play a significant role for increasing catalytic activity of Cu. These and other results from several surface and bulk sensitive methods shall be discussed in a bigger picture of the metal-support interactions and its infuence on the performance of Cu species for non-oxidative ammonia decomposition for CO_x-free H_2 production.

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DFT modelling and High-Resolution Solid-State NMR to identify γ-Alumina hydroxyls structure, location and spatial proximities

T. Pigeon [*1,2], A. T. F. Batista[1], J. Meyet[1], D. Wisser[1,2] M. Rivallan[1], D. Gajan[3] L. Catita[1], F. Diehl[1], A.S. Gay[1], C. Chizallet[1], A. Lesage[2], P. Raybaud[1, 3]

[1] *IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, 69360 Solaize (France)*
[2] *Université de Lyon, CNRS, ENS Lyon, Université Lyon 1, Centre de RMN à très haut champs de Lyon, UMR 5082, 5 rue de la Doua, 69100 Villeurbane (France)*
[3] *ENS Lyon, CNRS, Laboratoire de Chimie UMR 5182, 46 Allée d'Italie, 69364 Lyon (France)*
[*] *Email: thomas.pigeon@ifpen.fr*

Keywords: Gamma-alumina, surface models, edge models, DFT modelling

Introduction. γ-alumina is one of the most used catalyst support while the charaterization of its surface active sites still represents a challenge. Thanks to high field nuclear magnetic resonance (NMR), it becomes possible to identify the variety of hydroxyl groups and their proximities through ^{1}H-^{1}H dipolar correlation experiments. Nevertheless many proposed interpretations are still based on the exclusive consideration of ideal alumina surfaces. Thanks to density functional theory (DFT) simulations, we propose to revisit deeply this assignment by considering not only surface models but also edge models.

Experimental/methodology. DFT calculations of proton chemical shifts for various γ−alumina facet models ((100), $(110)_l$, $(110)_b$, (111))[1] and edge models ($(110)_l$/$(110)_b$, (100)/$(110)_b$, developped on purpose[2], and (100)/$(110)_l$[3]) were undertaken by using PBE functional with dDsC dispersion correction (VASP software). The gamma alumina samples PuralSB3 from Sasol, with various contents of chlorine, were treated at 500°C under H_2 for 2 hours and then conditionned under vacuo. The solid-state NMR spectra (^{1}H, ^{1}H-^{1}H 2D and ^{1}H-^{27}Al 2D) were acquired on a Bruker Avance III 18.8T spectrometer using 2.5mm zircone rotors and a magic angle spinning frequency of 30 kHz.

Results and discussion. We first show that the δ(^{1}H) = -0.1 ppm signal is attributed to the H-bond free μ_1-Al_{IV}-OH located at alumina edges as highlighted by the DFT models. Indeed, μ_1-Al_{IV}-OH species located on facets are systematically involved in H-bonds which deshield these protons to higher chemical shifts. Moreover, the ^{1}H-^{1}H auto-correlation observed at -0.1 ppm is corroborated by the (100)/$(110)_b$ edge model, while the one at 1.7 ppm can be attributed to μ_2-$Al_{VI}Al_{VI}$-OH present on the $(110)_b$ models. The cross correlations at -0.1 – 1.9 ppm and 2.1 – 3.1 ppm are attributed to H-bond free $\mu_1 - \mu_2$ and $\mu_2 - \mu_2$ in the edge vicinity. Adding 1.4 wt% chlorine induces the disappearance of 1D and 2D NMR peaks involving μ_1-Al_{IV}-OH species. This observation is explained by DFT calculations revealing a thermodynamically favored exchange of OH groups with chlorine at edges. Hence, this refined understanding provided in the present work will help to make new progress in the design of alumina supported catalysts thanks to a more rational tuning of facets and edges exposed according to the nature of hydroxyl sites targeted.

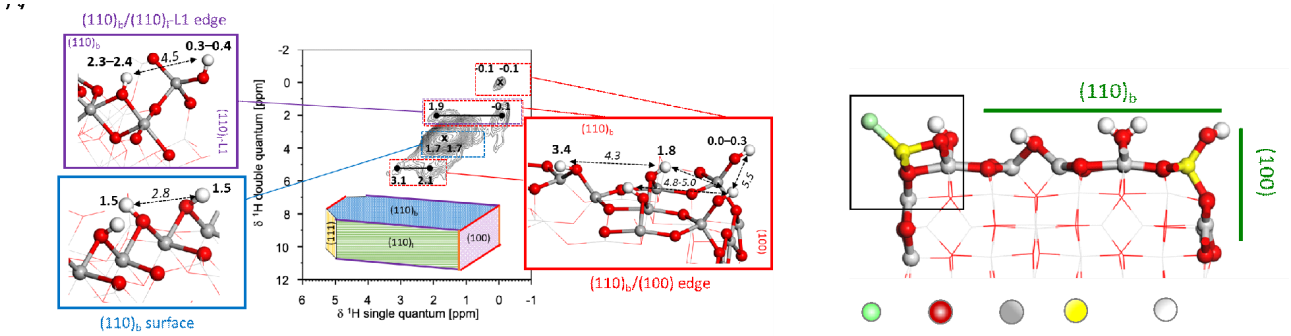

Figure 1: a) Most relevant DFT models of hydroxyls corroborating the correlations observed in the ^{1}H-^{1}H double quantum spectrum of γ-Al_2O_3. Calculated chemical shifts (in ppm) are reported as bold numbers and distances (in Å) in italic. **b)** DFT (110)/$(110)_b$ edge model exhibiting a μ_1-Al_{IV}-OH exchanged with chlorine in the frame.

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Insights in the water gas shift reaction over $CoFe_2O_4$ and $NiFe_2O_4$ based on operando spectroscopy techniques

M. Pittenauer[1*], R. Rameshan[1], F. Schrenk[1], C. Rameshan[1], K. Föttinger[1]

[1]*Technische Universität Wien, Vienna, Austria*
michael.pittenauer@tuwien.ac.at

Keywords: spinel ferrites, water gas shift reaction, operando spectroscopy, metal oxides, sol-gel synthesis

Introduction.

The water gas shift reaction is part of many industrial processes including steam reforming for adjustment of the ratio of CO/H_2 in syngas mixtures such as hydrogen production, synthesis of methanol and hydroformylation. Shifting from fossil syngas sources to renewable ones as well as technological diversity might justify further use of and research on the water gas shift reaction. The catalyst currently in use for high temperature water gas shift reaction (HT-WGS) is chromium-iron oxide doped with copper. Although this system has been optimized for a long time and research is relatively close to understanding the reaction mechanism [1], legislative initiatives require to find chromium-free catalysts for HT-WGS due to toxicity of Cr(VI). $CoFe_2O_4$ and $NiFe_2O_4$ have been chosen as initial candidates to conduct research upon as spinel compounds are reported to offer easy controllability and tunability of composition and chemical stability [2].

Experimental/methodology.

$CoFe_2O_4$ and $NiFe_2O_4$ samples have been prepared by a glycine-assisted sol-gel autocombustion process and structurally characterized by XRD and ATR-IR. Chemical reducibility as well as reactivity and possible parallel reactivity in HT-WGS have been investigated by H_2- and CO-TPR and temperature programmed reactions and phase changes determined by ex-situ XRD. CO conversion rates have been determined by GC. Insights in the reaction mechanism and the role of phase changes have been obtained by in-situ XRD, operando FTIR spectroscopy and NAP-XPS.

Results and discussion.

NAP-XPS revealed carbide-like species to be a relevant part of the reaction mechanism in agreement with the operando FTIR results showing no certain signs of any carbon species engaged in the WGS reaction. The stability of phase composition turned out to be limited in atmospheric pressure experiments as metallic phase formation occurs especially in $NiFe_2O_4$ according to both ex-situ and in-situ XRD results. As different types of carbides have been reported to act as catalysts in WGS [3, 4] and/or to play a role in reverse WGS respectively Fischer-Tropsch process, WGS reactivity of nickel and cobalt carbides has to be considered in future works.

Acknowledgments

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Spectroscopic Characterisation of Keggin-type Polyoxometalate Catalysts

Maximilian J. Poller[1*], Jan-Christian Raabe[1], Jakob Albert[1]
[1]*Institute for Technical and Macromolecular Chemistry at Hamburg University, Hamburg, Germany*
[*]*maximilian.poller@uni-hamburg.de*

Keywords: polyoxometalates, spectroscopy, transition metals, tailor-made catalysts

Introduction. The application of Keggin-type polyoxometalates in catalysis is an intensly researched field. Their high Brönsted acidity makes them excellent acid catalysts, and after introducing RedOx active transition metals into their structure, they can also be applied as oxidation catalysts. A prominent example for such catalysts are vanadium substituted phosphomolybdates, specifically $H_8PV_5Mo_7O_{40}$, which has been successfully applied for the conversion of biomass to formic acid.[1] In order to retain more valuable structures in oxidative biomass valorisation and to enable new processes, it is necessary to tailor the catalysts to the specific application. We have recently shown, that the incorporation of additional transition metals such as Mn(II) can be used to tune the RedOx potential of Keggin-type phosphomolybdates.[2] However, in order to further develop tailor-made catalysts, a more thorough understanding of such compounds is necessary. To this end we have synthesiszed various transition-metal substituted Keggin-type polyoxometalates and characterised them throughly in the solid state and in aqueous solution, with the aim of correlating molecular properties with their catalytic activity.

Experimental/methodology. We have investigated various transition metal substituted Keggin-type polyoxometalates in the solid state and in aqueous solution. For this purpose we emplyoed a wide range of analytical methods such as ATR-FT-IR spectroscopy, Raman spectroscopy, UV-Vis spectroscopy, NMR spectroscopy, and single-crystal x-ray diffraction.

Results and discussion. Vibrational spectroscopy and x-ray diffraction revealed the strucutral influence of the transition metals on the structure of the catalyst. NMR spectroscopy provided information on the behaviour of polyoxometaltes in solution, such as their dissociation behaviour (Figure 1).

$$[PM_xMo_{12-x}O_{40}]^{y-} + n\ H_2O \rightleftharpoons [PM_{x-1}Mo_{12-x}O_{40}]^{z-} + M_{aq}$$

Figure 1: Dissociation equilibrium of transition metal substituted Keggin-type polyoxometalate

UV-Vis spectroscopy showed the influence of the transition metal on the electronic excitation energies (i.e. HOMO-LUMO gap).

Correlation of these results with the catalytic activity of such polyoxometalates[3] will provide useful information for the further development of tailor made catalyst materials based on Keggin-type polyoxometalates.

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Is Ce^{3+}/Ce^{4+} redox necessary: Extreme high CO conversion at non-reducible CeO_2 surface

Yifei Ren**,[a] , Hao Gu,[a] ,Xuze Guan,[a] Zhangyi Yao,[a] Meiyao Wu,[b] Chunjiang Jia,[b] Feng Ryan Wang[a]*

a) Department of Chemical Engineering, University College London, Roberts Building, Torrington Place, London WC1E 7JE, UK

b) Key Laboratory for Colloid and Interface Chemistry, Key Laboratory of Special Aggregated Materials, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

** email: ryan.wang@ucl.ac.uk.*

*** email: yifei.ren.15@ucl.ac.uk.*

Introduction.

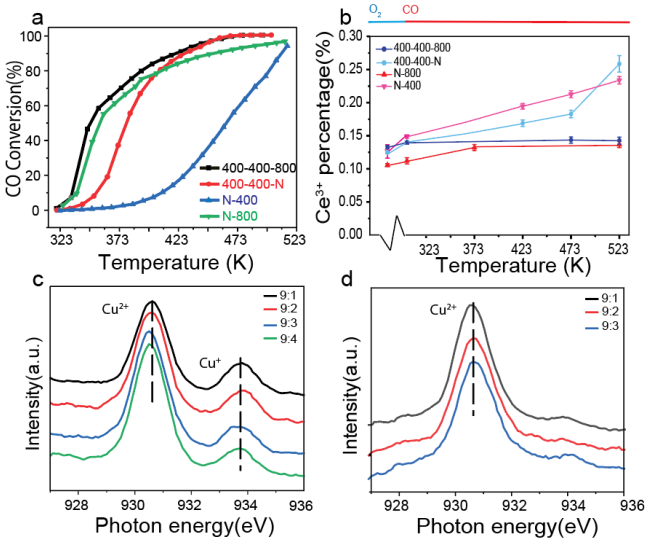
In heterogeneous catalysis research, CO oxidation reaction ($2CO+O_2 \square 2CO_2$) is a well-known reaction for fundamental mechanism study, as well as a vital reaction in terms of environmental pollution derived from various of sources, especially from vehicle exhaust. In CO oxidation reaction, it is widely acknowledged that the redox of Ce^{4+}/Ce^{3+} pair and the surface O_2- mobility is the key to achieving a high CO conversion. However, we have discovered a Cu-CeO_2 system with non-reducible CeO_2 surface at 523 K, has an extremely high CO conversion after calcined at 1073 K in air (Fig. 1a). Such massive improvement in catalysis encourages us using various methods to investigate the reason behind it, providing a different point of view towards the electronic metal support interaction (EMSI) theory.

Experimental/methodology.

All the chemicals were of analytical grade without further purification. The ceria nanorods were prepared by a hydrothermal method. Then, the catalysts were prepared by a deposition−precipitation method. Catalytic activity tests were performed from room temperature to 250 °C with 1% CO, 10% O_2 and balance He. The analysis of the Cu K-edge (8.979 keV) and Ce L3-edge (5.723 keV) was performed at 3.0 GeV with a beam current of 300 mA at the Beamline B18 of the Diamond Light Source (UK). The in-situ measurements were accomplished in the ambient pressure Xray end-station using a Faraday-cup to collect the NEXAFS spectra in the Ce M-edge and Cu L3-edge at different gas compositions at the ISISS beamline of BESSY II in Berlin (Germany), and the beamline B07 of the Diamond Light Source.

Results and discussion.

To prevent Ce^{4+} participating the reaction, we have calcined the CuO-CeO_2 system at 1073 K, reducing its oxygen vacancy, Ce^{4+} in the calcined sample (400-400-800 and N-800) cannot be reduced to Ce^{3+} even at 523K in pure CO (Fig. 1b). Therefore, we believe that the surface Cu species is the key for high CO conversion at low temperature, which tends to keep Cu^+ with O2 existence. This theory is also confirmed by the Cu L-edge spectra for the uncalcined sample(Fig. 1d), which shows the majority of Cu are oxidised when O_2 is introduced at 373 K. Cu K-edge spectra also shows a similar result, where the linear combination fitting shows a higher percentage of Cu and Cu^+ in the bulk with pure CO and different CO: O_2 ratio under 373 K for the calcined sample, comparing with the uncalcined sample in pure CO under the same temperature.



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In the catalytic field, the result will directly challenge the support redox and EMSI theory. It suggests that an efficient catalyst does not require an active support but a unique active site structure, providing a new perspective of catalyst design.

Figure 1 (a) CO conversion (b) Peak fitting results of Ce^{3+} percentage under O_2, 30C and CO in different temperatures (c) Cu L3 edge NEXAFS spectra of 400-400-800 and (d) 400-400-N at 373K with different CO: O_2 ratios.

Comparative study of the aging time of Cu/TiO_2 catalysts: effect of the preparation method

A. J. Reynoso[1,2], L. Djakovitch[1], S. Loridant[1], T. Epicier[1], N. Perret[1]

[1]*IRCELYON, Univ Lyon, Université Claude Bernard Lyon 1, CNRS, 69626, Villeurbanne, France*
[2]*Dept. of Chemical Engineering, Faculty of Science and Technology, UPV/EHU, 48940 Leioa, Spain*
[*]*noemie.perret@ircelyon.univ-lyon1.fr*

Introduction. Copper-based catalysts are widely used in important industrial applications, such as water-gas shift reaction, synthesis of methanol from CO_2, and alcohols production from esters, selective hydrogenation of oils, among many others. The performances of catalysts are closely related to the copper dispersion and particles size [1]. Therefore, preparation method is a crucial step to have active, selective and stable catalyst system. Wet impregnation is a widely employed procedure for preparation of Cu nanoparticles. However, high-temperature H_2 reduction process could cause the aggregation of Cu particles. As an alternative, one-pot aqueous reduction method is simple, with limited equipment requirements, ease of control and small nanoparticles size can be obtained [2].

The metallic state of Cu is unstable in air. Depending on the storage conditions the metal will be partly or completely re-oxidized to its stable oxides causing catalyst deactivation. In order to restrain this phenomenon, passivation is commonly carried out. Nevertheless, although reactivation can be conducted in-situ under H_2, re-oxidation of the catalyst during storage inevitably occurs over time [3]. In this work, a comparative study on the stability of Cu/TiO_2 catalysts synthesized by either aqueous reduction method or wet impregnation followed by H_2 reduction was carried out.

Experimental/methodology. Cu/TiO_2 (10 wt.%) was prepared by either one-pot aqueous reduction method using sodium borohydride as a reducing agent (R-$NaBH_4$) and by wet impregnation method followed by reduction under H_2 flow and passivation (R-H_2). After synthesis, the samples were stored under air.The catalysts were periodically characterized over several months by ICP, XRD, XPS, H_2-TPR, N_2 physisorption, N_2O chemisorption, Raman, and TEM-EELS. Catalytic activity was evaluated in 2-octanol acceptor-less dehydrogenation. The reaction was performed in semi-bath reactor with constant flow of inert gas.

Results and discussion. Just after synthesis (t_0), the sample prepared by $NaBH_4$ reduction process exhibited better dispersion and greater metallic surface than catalyst reduced under H_2 flow (25.2 m^2/g_{Cu} for R-$NaBH_4$ vs 13.6 m^2/g_{Cu} for R-H_2). By Raman, bands attributable to Cu_2O (216 and 106 cm^{-1}) were observed for sample R-$NaBH_4$. After two months (t_2), both samples showed bands at 297 cm^{-1}, characteristic of CuO. Regarding catalytic activity, R-$NaBH_4$ presented slightly higher conversion and yield than its counterpart (Fig. 1). Results after 4 months will also be presented in detail.

In short, a faster reoxidation process was revealed on R-$NaBH_4$ compared to R-H_2 catalysts. Nonetheless, catalytic activity is totally recovered with an in situ H_2 pretreatment at low temperature (145 °C).

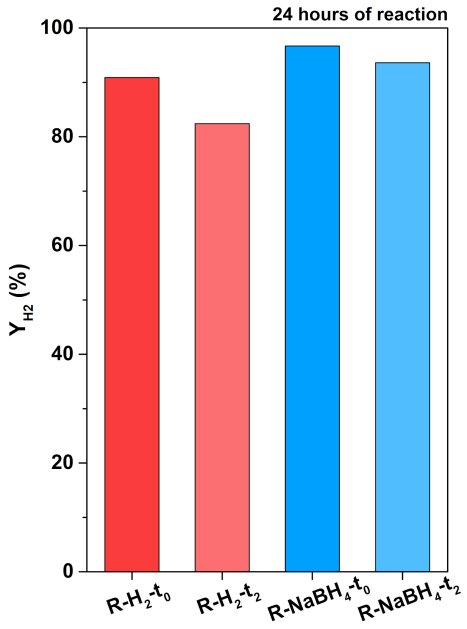

Fig. 1. H_2 yields in 2-octanol dehydrogenation.

Acknowledgments

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Is Ce^{3+}/Ce^{4+} redox necessary: Extreme high CO conversion at non-reducible CeO_2 surface

Yifei Ren**,[a] , Hao Gu,[a] ,Xuze Guan,[a] Zhangyi Yao,[a] Meiyao Wu,[b] Chunjiang Jia,[b] Feng Ryan Wang[a]*

a) Department of Chemical Engineering, University College London, Roberts Building, Torrington Place, London WC1E 7JE, UK

b) Key Laboratory for Colloid and Interface Chemistry, Key Laboratory of Special Aggregated Materials, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

** email: ryan.wang@ucl.ac.uk.*

*** email: yifei.ren.15@ucl.ac.uk.*

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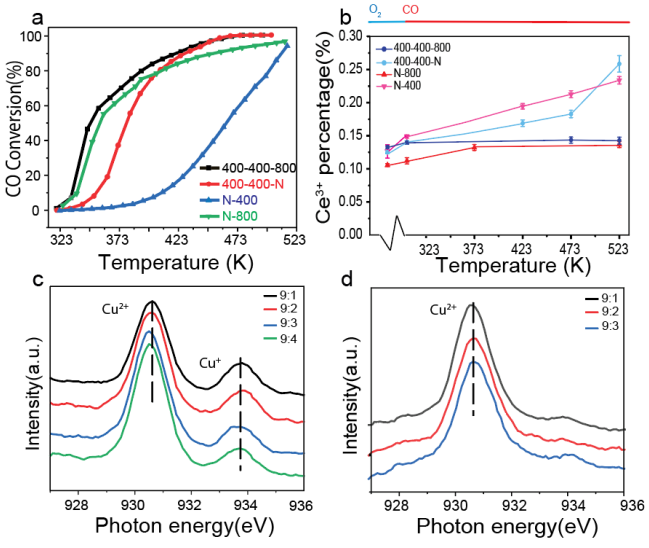

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Study of active sites involved in the oxidative dehydrogenation of propane via boron nitride

M. Sajad[1*], K. Knotková[1], S. Šlang[2], M. Rubeš[1], R. Bulanek[1]

[1]*The University of Pardubice, Department of Physical Chemistry, Pardubice, Czech Republic*
[2]*The University of Pardubice, Center of Materials and Nanotechnologies, Pardubice, Czech Republic*
[*]*Mehran.sajad@upce.cz*

Introduction.

The global demand for light olefins, such as propene, is continually increasing as they are critical precursors for chemical manufacturing. Light olefins are mainly produced via steam cracking of naphtha and fluid catalytic cracking of crude oil, but there are several limitations, e.g., high temperature, significant CO_2 emission, coke formation, etc. Therefore, discovering new catalysts to increase production efficiency is an essential area of research. Oxidative dehydrogenation (ODH) is one of the promising approaches that has been studied for more than two decades. The advantages of ODH over the non-oxidative method are lower operating temperature, exothermic nature, no equilibrium limit, and no coke formation. But, the challenge is finding a stable catalyst with high activity and selectivity while avoiding overoxidation [1, 2].

Experimental/methodology.

In this work, hexagonal boron nitride (hBN), as a recently reported promising nonmetallic catalyst [3], has been studied in the oxidative dehydrogenation of propane (ODHP). The fresh and spent catalysts were characterized by X-ray diffraction (XRD) patterns, energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), N_2 adsorption-desorption isotherms, Raman, and infrared spectroscopy to monitor the chemical changes and the formation of various functional groups in the spent catalysts. DFT calculations were performed on small model clusters of boron-oxide to investigate FT-IR features upon CO adsorption.

Results and discussion.

It is widely acknowledged that the BO_x species, which are generated by substituting N with O, are the possible core triggers of the catalytic process. However, views on the actual active sites and the catalytic mechanism are still controversial. In this research, the participation of oxygen within the hBN structure and formation of BO_x were studied as well, but all of the observed phenomena did not influence the catalyst activity, which brings the question of whether the BO_x are truly active sites or not. Impregnation of h-BN with boron oxide proved that the presence of boron oxide on the h-BN surface suppresses the activity of the catalyst, whereas it was recovered by washing the catalyst and removing the boron oxides. Thus the BO_x probably is different from the actual active site. On the other hand, it has already been experimentally and theoretically evidenced that gas-phase reactions play a critical role in this system [4, 5]. Here the experiments show how larger available space can influence radical propagation and productivity. Also, the role of the catalyst surface was investigated with CO adsorption monitored by IR spectroscopy that showed negligible interaction between CO and the BN surface. However, unsaturated boron sites should form a dative bond with CO, as evidenced by model cluster calculations. It disclosed that coordinatively unsaturated boron is not available on the hBN surface or is formed under the elevated temperature of the reaction process (~400 °C). The presented results suggest that the reasons for the unusual activity of h-BN in the ODH of propane should be sought elsewhere than in the presence of boron oxide.

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Dynamics of nanoparticle motion and metal-oxide support in redox-reactive gases

Arik Beck[1]*, Hannes Frey[1], Xing Huang[3], Marc-Georg Willinger[2], Jeroen A. van Bokhoven[1,4]

[1]*ETH Zurich, Vladimir-Prelog-Weg 1-10, 8093 Zurich (Switzerland)*
[2] *TUM Technical University Munich, Lichtenbergstraße 4, 85748 Garching (Germany)*
[3]*College of Chemistry, Fuzhou University, Fuzhou 350116 (P. R. China)*
[4]*Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen (Switzerland)*
**arik.beck@chem.ethz.ch*

Keywords: Pt/TiO_2, dynamics, in-situ TEM, strong metal-support interactions

Introduction

In the early days of catalysis research, oxide carriers were considered to be mere inert carriers for highly dispersed metal nanoparticles. Forty years ago, experiments with noble metal-TiO2 catalysts demonstrated that oxide supports are far from inert in such catalytic systems and can strongly effect the adsorption behavior and structure of catalysts and the phenomenon was named the strong metal-support interaction (SMSI) [1]. SMSI was observed in noble metal catalysts supported on reducible oxides such as TiO2. This phenomenon is of paramount importance, since it can determine the catalytic activity and stability. The SMSI phenomenon has, for the most part, been characterized ex situ. Such an approach is not able to capture the ongoing dynamics of a working system. The dynamic interactions between noble metal particles and reducible metal-oxide supports can depend on redox reactions with ambient gases.

Results and Discussion

In our work [2,3], operando transmission electron microscopy revealed that the SMSI–induced encapsulation of platinum particles on TiO2 observed under reducing conditions is lost once the system is exposed to a redox-reactive environment containing oxygen and hydrogen at a total pressure of ~1 bar. Destabilization of the metal–oxide interface and redox-mediated reconstructions of TiO2 lead to particle dynamics and directed particle migration that depend on nanoparticle orientation (Figure 1). A static encapsulated SMSI state was reestablished when switching back to purely oxidizing conditions.

Significance

This work highlights the difference between reactive and nonreactive states and demonstrates that manifestations of the metal-support interaction strongly depend on the chemical environment.

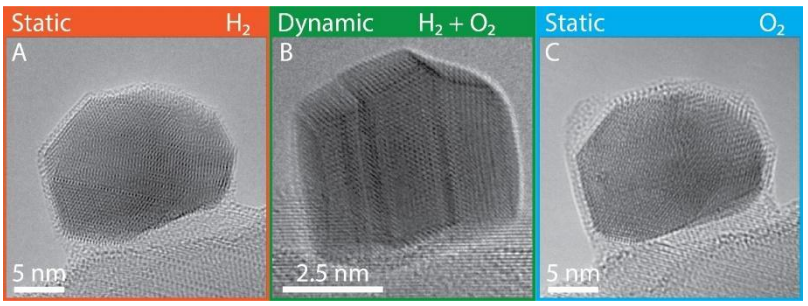

Figure 1. In situ TEM micrographs of the platinum titania system at elevated temperature. A under hydrogen atmosphere, B under hydrogen oxygen mixed feed, C under oxygen atmosphere.

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Combined XAS and DRIFT Spectroscopic Investigation to Unravel the Dynamic Structural Evolution of Supported Atoms and Clusters

Bidyut Bikash Sarma[1,2,3], Jelena Jelic[2], Dominik Neukum[2], Dmitry E. Doronkin[1,2], Xiaohui Huang[4], Felix Studt[1,2] and Jan-Dierk, Grunwaldt[1,2]

[1]*Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstraße 20, 76131 Karlsruhe, Germany;* [2]*Institute of Catalysis Research and Technology, KIT, Hermann-von Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany;* [3] *Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Rd, Cambridge CB2 1EW United Kingdom,* [4]*Institute of Nanotechnology, KIT, Hermann-von-Helmoltz Platz 1, 76344, Eggenstein-Leopoldshafen, Germany. Emai:bidyut.sarma@kit.edu; bbs25@cam.ac.uk*

Introduction. An emerging field in heterogeneous catalysis is to understand the dynamic behavior of atoms and clusters over solid supports. In many catalytic processes that were reported to be catalyzed by nano-particles, recent studies show that single atom or ultra-small clusters are attractive as active species. However, under reaction conditions, stability of single atom is questionable and transformation between atoms and clusters is observed during *in-situ*/operando spectroscopic investigations.[1][2] To unravel the structural evolution of atoms and clusters of late transition metals (Ru, Rh, Pd, Ir and Pt) supported over CeO_2, we propose here *in-situ* X-ray Absorption Spectroscopy (XAS) and Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy (CO as probe molecule) as powerful tools. In addition, DFT calculations were carried out to accurately predict the CO vibrational frequencies of the species evolved under reaction conditions. This study shows a general trend of late transition metals over CeO_2 in CO adsorption energies with CO absorption frequencies over single atom catalysts bearing various charges.[3]

Experimental/methodology. All the catalysts were synthesized by wet impregnation and precipitation methods. The catalysts were calcined at 1073 K and 623 K respectively in static air. The synthesized catalysts were characterized by powder XRD, Raman spectroscopy, N_2-physisorption, C_s-STEM, XAS and DRIFT spectroscopy. *In-situ* XAS and DRIFT spectroscopy were conducted under the gas flow of 1% CO, 1% CO + 1% O_2 and 1% CO + 1% H_2 balanced with He or Ar.

Results and discussion. The *ex-situ* characterization of the synthesized catalysts prepared by the two methods showed that the catalysts are mostly in atomically dispersed state over CeO_2. The *in-situ* DRIFT and XAS spectra measured under different reaction conditions showed the species evolved with time and temperature. As an example, the results of the Rh/CeO_2 catalysts are shown in figure 1. Two CO vibrational frequencies in the ranges between 2000-2020 cm^{-1} and 2070-2090 cm^{-1} were observed (figure 1(c)) which corresponds to the anti-symmetric and symmetric vibrational frequencies of the geminal dicarbonyl species adsorbed over Rh single atoms. Upon changing the gas mixture to CO + O_2, a new CO vibrational frequency at 2107 cm^{-1} appeared which can be assigned to CO adsorbed over Rh^{3+} species. On the other hand, when the gas mixture was switched to CO + H_2 at 453 K, a new CO vibrational frequency is observed at 2046 cm^{-1}, which can be attributed to CO adsorbed over Rh clusters or nano particles. DFT calculated CO vibrational frequencies match with the experimental results. The temperature programmed XAS spectra collected at the Rh K-edge also show that the Rh single atom catalyst forms clusters at elevated temperature in the presence of CO + H_2. These results are highly interesting and will pave the way for future design of new catalysts for industrially relevant reactions such as hydroformylation, higher alcohol synthesis and acetic acid production.

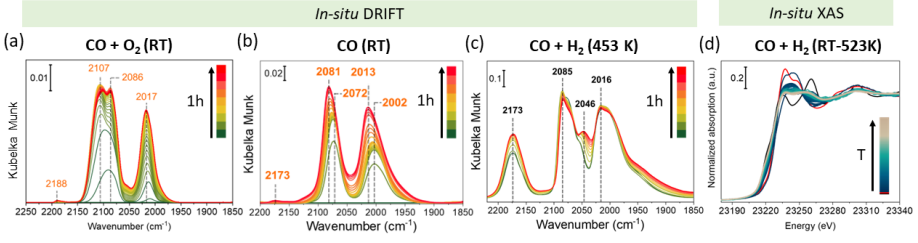

Figure 1. *In-situ* DRIFT spectra of Rh_1/CeO_2 catalysts measured during (a) CO + O_2, (b) CO and (c) CO + H_2 reaction conditions. *In-situ* XAS spectra measured at the Rh K-edge under CO + H_2 are shown in figure (d). Temperatures are shown within the parentheses. The *in-situ* DRIFT spectra were collected over 1 hour.

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Visualising Sulphur Poisoning in Structured Honeycomb Catalysts with Hard X-ray Nanotomography

S. Sharma[1], T. Delrieux[1], D. Karpov[2], M. Casapu[1], J.-D. Grunwaldt[1], T.L. Sheppard[1]*

[1]*Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany*
[2]*European Synchrotron Radiation Facility, 38000 Grenoble, France*
[*]*thomas.sheppard@kit.edu*

Keywords: characterisation, spatially-resolved, synchrotron radiation, X-ray tomography

Introduction. Technical CH_4 oxidation catalysts for removal of unburned hydrocarbons in emissions control applications are usually composed of metal or ceramic substrates with a washcoat of catalytic material. Mass and heat transport limitations in these hierarchical structures bring additional complexity compared to model systems. Depending on feedstock (e.g. diesel, natural gas engines) such catalysts may suffer strong deactivation from sulphur poisoning. This may not only trigger molecular changes in the catalyst, but also affect transport properties by sulphur deposition and blockage of pores and active sites.[1] Moreover, concentration gradients can develop within the washcoat and along the monolith channels. Identifying the location of sulphurous species and the severity of poisoning in structured catalysts is key to understanding the poisoning mechanism and its impact on catalyst performance, later including strategies for catalyst regeneration.[2,3] Hard X-ray nanotomography offers a flexible characterisation toolbox which can be used to observe and quantify local deactivation effects of technical catalysts in 3D space.[4,5]

Experimental/methodology. Coated 1.6wt% Pd/Al_2O_3 catalyst honeycombs were poisoned in SO_2-containing gas feed for various time on stream, and regenerated by short exposure to 2% H_2, mimicking fuel-lean operating conditions of CH_4 combustion engine followed by fuel-rich catalyst regeneration, similarly as in ref. [3]. Honeycomb catalysts with different degrees of sulphur poisoning and regeneration were then studied by hard X-ray holotomography at ESRF synchrotron, beamline ID16A. Catalyst volumes up to 280x280x100 μm^3 were studied with spatial resolution estimated at a few hundred nm.

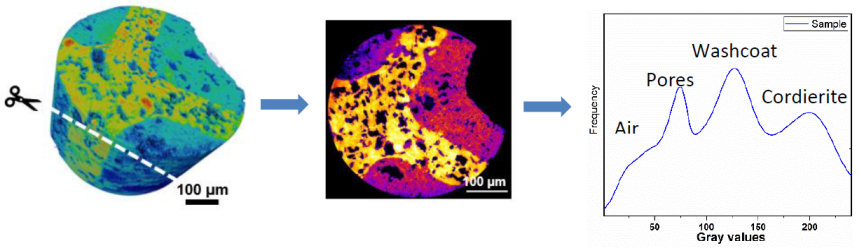

Figure 1. Volume (l), cross-section (m), and electron density histogram (r).

Results and discussion. Hard X-ray holotomography is shown as a powerful nanoscale imaging method which allows quantitative analysis of the local electron density in the sample,[6] indicating the presence and severity of sulphur deposition. Sufficient contrast allowed to distinguish between alumina honeycomb, open pores, and dense sulphur deposits in the monolith channel and corner sections (Fig. 1). Sulphur deposition was visualised by increased electron density in the washcoat as well as honeycomb support compared to a fresh catalyst. This effect increased together with poisoning duration, and was non-uniform along the monolith channel, with the reactor inlet more severely poisoned than the outlet. Partial structural regeneration was confirmed by loss of electron density (i.e. sulphur deposits) after treatment in H_2 feed. The results help to understand the basis of sulphur poisoning and regeneration of technical catalysts, promoted by direct visualisation of such effects with tomography. Only hard X-ray tomography at synchrotron radiation sources is capable of providing 3D spatially-resolved data on extended samples with nm-scale resolution.

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Hard X-ray tomography reveals structural degradation and chemical composition of Pt/Rh gauze catalysts for NH_3 oxidation

S. Das[1], M. Stuckelberger[2], J. Pottbacker[3], S. Jakobtorweihen[3], R. Horn[3], T. L. Sheppard[1]*

[1]*Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany;* [2]*Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany;* [3]*Hamburg University of Technology (TUHH), Hamburg, Germany*
[*]*Corresponding author: thomas.sheppard@kit.edu*

Introduction

Large-scale catalytic production of nitric acid is industrially carried out over smooth Pt-alloy gauze catalysts. During this exothermic process, the surface of catalyst undergoes deformation and reconstructs into cauliflower-like structures[1,2]. This results in material loss, decrease in catalyst activity and reaction selectivity, eventually leading to failure of the catalyst[3]. Despite several decades of industrial operation for Pt/Rh gauze catalysts in NH_3 oxidation, the significant potential for wastage of valuable noble metals remains unresolved. In this study, hard X-ray tomography was used to visualise the degradation and quantify the elemental composition of Pt/Rh gauzes, providing a 3D spatially-resolved visualisation of catalyst degradation during NH_3 oxidation in a bench-scale setup.

Experimental/methodology

Industrial Pt/Rh gauzes of ca. 76 µm diameter were aged under realistic reaction conditions for NH_3 oxidation using a bench-scale reactor setup at TUHH Hamburg[4]. To monitor the degradation of catalyst material as a function of reaction time, single wires extracted from aged gauzes were studied to understand the structural and compositional changes using non-invasive *ex situ* 3D scanning transmission X-ray tomography (STXM-CT)[5]. Experiments were performed at P06 beamline of PETRA III synchrotron radiation source (DESY, Hamburg) at resonant energies, i.e. above and below Rh K-edge (23.300 and 23.208 keV).

Results and discussion

High resolution STXM-CT performed with a spatial resolution of ca. 2 µm allows for morphological studies extending beyond surface information. Furthermore, on-off resonant energy measurement, via Beer-Lambert's law, provides information regarding the 3D spatial chemical distribution of Pt and Rh in the wires as a function of reaction time. With increasing reaction time, significant loss of bulk catalyst material was observed [Fig. 1a]. This was accompanied by increase in size of porous cauliflower structures. The chemical distribution study shows correlated higher Pt distribution in the wire core compared to the cauliflower-like structures on the outer surface, confirming Pt loss from the surface of the wires. At the same time, Rh enrichment was validated in the outer rim of the wire structure and cauliflowers [Fig. 1b]. Understanding how to mitigate material loss and improve catalyst stability is essential for catalyst development. Advanced catalyst characterization such as tomography with chemical contrast imparts unique insights into the structure and composition of such challenging samples, which are unavailable using contemporary methods.

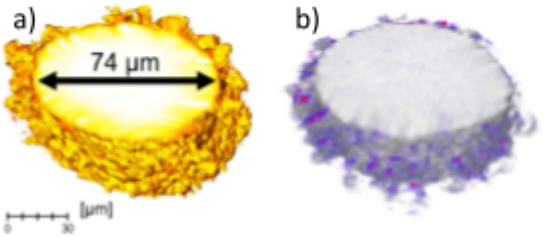

Figure 1: a) Tomographic reconstruction showing structurally degraded Pt/Rh wire after 24h time on stream for NH_3 oxidation, and b) its computed Pt (grayscale) and Rh (color) distribution

Acknowledgments

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Elucidating the Role of Bismuth as a Promotor Element on the Pt-Catalyzed CO Oxidation Reaction

J. Siewe[1], E.T.C. Vogt[1], B.M. Weckhuysen[1,*]

[1] Inorganic Chemistry and Catalysis group, *Debye Institute for Nanomaterials Science & Institute for Sustainable & Circular Chemistry, Utrecht University, Utrecht, the Netherlands*
[*] *b.m.weckhuysen@uu.nl*

Keywords: *Operando* DRIFTS, CO Oxidation, Bismuth, Promotion Effects, Pt/Al_2O_3

Introduction. The oxidation of CO is a quintessential system to understand the elementary surface reactions taking place on catalyst materials.[1] Furthermore, since CO is often present as a poisonous impurity in automotive exhaust gases, the catalytic process also has environmental impact. Adding bismuth as a promotor element to supported Pt nanoparticles (NPs) has been found to improve catalyst stability and lowers the temperature at which 50% of CO is converted, $T_{50\%}$, by 20–90 °C.[1,2] The underlying reason for the promoting effect of Bi is not yet well understood. In this work, light has been shed on the promoting effect of Bi by monitoring the surface properties of Pt NPs during catalytic CO oxidation using *operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

Experimental/methodology. *Operando* DRIFTS CO oxidation was performed in a Harrick cell using a Brüker Tenser II and an online GC. The Pt/(Bi-)Al_2O_3 catalyst materials, which were provided by Umicore, were pretreated at 600 °C in O_2 atmosphere. The CO oxidation reaction was performed by heating the cell with 1 °C/min up to 400 °C in 1000 ppm CO. X-ray photoelectron (XPS) analysis was performed using a ThermoFischer K-alpha X-ray based XPS system.

Results and discussion. In *operando* DRIFTS CO oxidation experiments, a redshift of the linearly bonded CO peak was observed, from 2090 cm^{-1} to 2080 cm^{-1} upon promotion (Figure 1b), which coincided with a 45 °C decrease of the $T_{50\%}$ (Figure 1a). Furthermore, the promoted sample retained a higher CO coverage at the same CO conversion rates, compared to the Pt-only catalyst, as is shown in Figure 1c. There was a notable absence of the bridge bonded CO peak in Figure 1b, which could indicate electronic changes to the Pt NPs. Structural characterization by XPS, as shown in Figure 1d, revealed a shift of the Pt 4d bands of 0.5 eV upon Bi promotion, suggesting that the Pt NPs are in a slightly more oxidized state. Furthermore, Figure 1e shows that Bi is significantly more oxidized in the presence of Pt as Bi^{3+} contributions could be revealed.

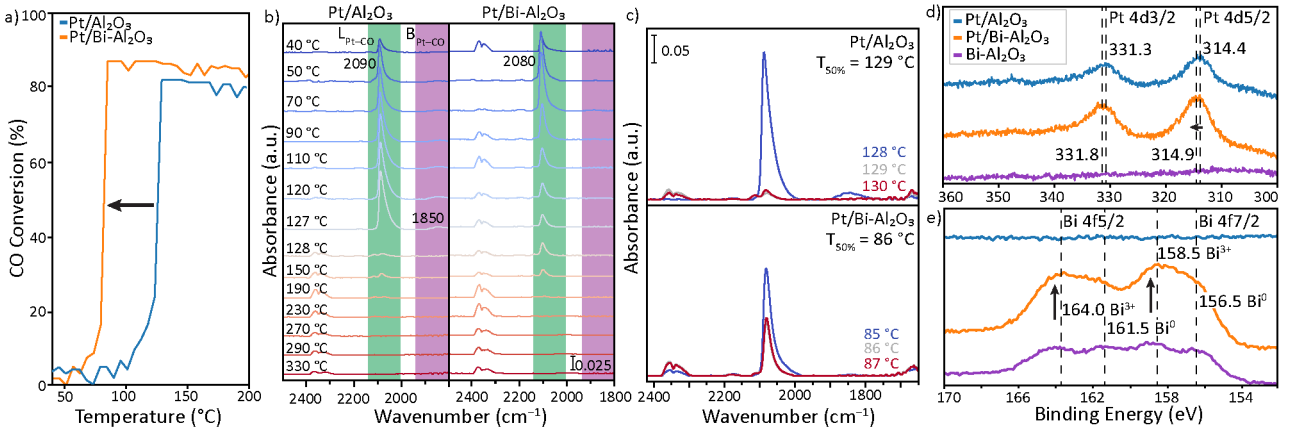

Fig. 1 a) CO conversion as a function of temperature measured during *operando* CO oxidation, b) DRIFTS spectra at specified temperatures taken during *operando* CO oxidation, c) DRIFTS spectra at $T_{50\%}$ & d-e) XPS spectra of the Pt 4d and Bi 4f.

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Reconstruction of the ZnAl mixed oxides into the layered double hydroxide catalysts active in the aldol condensation of furfural

Lada Dubnová[1], Rostislav Daňhel[1], Vendula Meinhardová[1], Valeriia Korolova[2], Lucie Smoláková[1*], Tomasz Kondratowicz[1], Oleg Kikhtyanin[2] and Libor Čapek[1]

[1]*Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Pardubice, Czechia*

[2]*Technopark Kralupy VŠCHT Praha, University of Chemistry and Technology Prague, Prague, Czechia*

[*]*lucie.smolakova@upce.cz*

Keywords: ZnAl reconstructed LDHs, temperature programed techniques, in-situ DRS, structural properties, basic properties, aldol condensation of furfural

Introduction. RE-LDHs are characterized by higher activity of the given materials in base-catalysed reactions than original LDHs [1]. The reason for the increased activity could be a change in the basic properties of the RE-LDHs associated with the formation of more Brønsted basic OH^- sites in the interlayer space, instead of the original CO_3^{2-} anions contained in the original LDHs and released from the materials during calcination to mixed oxide [2]. OH^- ions are incorporated into the mixed oxide layers. It changes the Lewis basic sites (medium Zn-O and Al-O sites and strong O^{2-} sites) of the mixed oxide to Brønsted (typically between these include OH^-) basic sites of RE-LDHs [3].

Experimental/methodology. ZnAl LDHs were prepared by three different methods (coprecipitation method using Na_2CO_3 as a buffer, using NaOH as a buffer and using hydrolysing urea), of them the corresponding mixed oxides and RE-LDHs were subsequently prepared. Materials were characterized by XRD, TPD-CO_2 and in-situ diffuse reflectance spectroscopy. Their activity was studied in aldol condensation of fufural.

Results. The main goal was to describe the so-called memory effect in ZnAl RE-LDHs. The individual preparations differed fundamentally in the ZnAl properties of the RE-LDHs. The most fundamental differences can be seen in content of well-crystalline ZnO phase, ability to reconstruct the LDH structure and content of basic sites. All ZnAl RE-LDHs contained both LDH and ZnO structure. The content of well-crystalline ZnO phase depended on the type of synthesis and it increased with increasing Zn/Al molar ratio. Its content was higher in ZnAl RE-LDHs than in corresponding ZnAl LDHs and it was present even in materials originating from ZnAl LDH with pure LDH structure. The content of well-crystalline ZnO phase was lower in ZnAl RE-LDH originated from coprecipitation method of LDH synthesis using hydrolysing urea than from coprecipitation method of LDH synthesis using NaOH or Na_2CO_3 as a buffer. Repeated number of the reconstruction of LDH structure led to the increase content of well-crystalline ZnO phase that possess smaller crystallite size, the increasing width of the space between the layers, decreasing interaction of the interlayer CO_3^{2-} groups with LDH structure and increasing content of weak basic sites. Although LDH structure recovery is slower in gas phase than in liquid phase, the prolong time in gas phase leads to the similar LDH structure recovery as in liquid phase. ZnAl Re-LDHs possed significantly higher furfural conversion than ZnAl mixed oxides.

Acknowledgments

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Surface photovoltage application for revealing carrier transfer behaviour and photocatalytic mechanisms in photocatalyst systems

K. Spilarewicz[1*], A. Jakimińska[2], K. Urbanek[2], W. Macyk[1]

[1] *Faculty of Chemistry, Jagiellonian University, ul. Gronostajowa 2, Kraków, 30-387, Poland*
[2]*Doctoral School of Exact and Natural Sciences, Jagiellonian University, Łojasiewicza 11, 30-348 Kraków, Poland*
[*]*kaja.spilarewicz@uj.edu.pl*

Keywords: photocatalysis, heterojunction, SPV, mechanism

Introduction. The design of heterojunctions by coupling two semiconductors together is a promising way to achieve high photocatalytic activity by inducing photogenerated charge separation. The surface photovoltage measurement can be a very efficient tool for the verification of p- or n-type conductivity of separate photocatalysts. Moreover, if the semiconductors are coupled in the form of layers, the direction of the photogenerated charge transfer can be monitored using this technique [1]. Therefore it can be applied to determine a junction's existence and provide tips for photocatalytic mechanism enlightenment.

Experimental/methodology. The photocatalysts systems were designed for CO_2 reduction and water-splitting/methanol photoreforming. The materials used for measurements were standard photocatalysts (*e.g*. P25, anatase) and as-synthesized by wet methods (precipitation, hydrothermal). After verification of their photocatalytic activity, the mechanism was studied using the Kelvin probe (surface photovoltage as the change of contact potential difference during pulsed irradiation in monochromatic light) and additionally supported by spectroelectrochemical measurements (SE-DRS).

Results and discussion. Surface photovoltage was measured for separate materials, mixed together and as layered coatings ("sandwich" type). The efficient junction can be observed as an increased absolute contact potential difference (CPD) after the coupling of both materials. The direction of the charge transfer between them was verified by preparing materials coupled layer by layer in inverse order. For example, an effective heterojunction was found for ZFO-TiO_2 ($ZnFe_2O_4$-anatase) tandem, which was designed for photocatalytic CO_2 reduction – Figure 1. Moreover, the applied methodology enables us to revise the well-known TiO_2-Ag_2O system (used *i.a.* for water-splitting), revealing no junction between both materials [2].

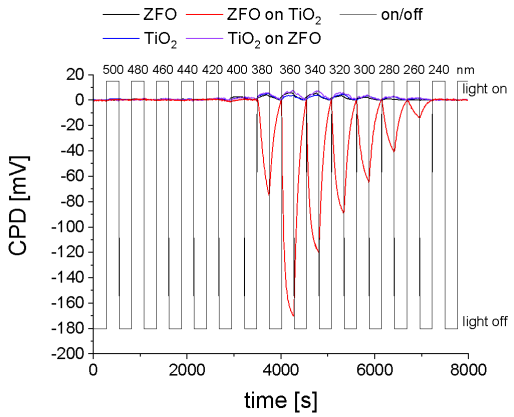

Fig.1. Surface photovoltage for $ZnFe_2O_4$-anatase photocatalytic system.

Acknowledgements

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Toolkit for the Structural Characterization of Mesoporous Zeolite Catalysts

Katie Cychosz Struckhoff[1*]; Matthias Thommes[2]

[1]*Anton Paar Quantatec, Boynton Beach, FL, USA*
[2]*University of Erlangen-Nuremburg, Erlangen, Germany*

Introduction.
Much effort has been devoted to the development of materials which exhibit hierarchical pore structure with advantageous micro- and mesopore connectivity. The network of interconnected pores facilitates efficient transfer of fluids to and from catalytically active sites, leading to benefits in numerous catalytic applications. A large amount of work has been dedicated to their pore structural characterization [1]. Detailed insights into the pore architecture (pore size distribution, pore volume and pore interconnectivity) are important because they control transport phenomena, diffusional rates, and govern selectivity.
Gas sorption is well suited for this because it assesses a wide range of pore sizes [2]. An in-depth characterization of the pore network can also be obtained with a detailed understanding of the adsorption and phase behavior of fluids confined in such complex pore structures. Here, a toolkit of recommended experimental and state-of-the-art data reduction methods for a comprehensive study of the pore architecture is provided.

Experimental/methodology.
Adsorption experiments were performed using a Quantachrome autosorb-iQ MP. Prior to the adsorption experiments, samples were degassed for 12 h at 623 K under turbomolecular pump vacuum.

Results and discussion.
Each tool for characterization of mesoporous zeolites has been validated using recent examples, which will be discussed in detail. Tools include:
(1) *Argon (87 K) adsorption* is recommend by IUPAC for accurate characterization of polar materials.
(2) *NLDFT methods for pore size* allow one to obtain a complete and accurate micro- and mesopore size distribution. Argon (87 K) adsorption coupled with NLDFT methods have been applied to a series of mesoporous Y zeolites (Figure 1) [3].
(3) *Comparison of isotherms measured using different adsorptives* (N_2 and Ar) to obtain pore network information.
(4) *Varying measurement temperature to* change the state of the confined pore fluid. Argon (77 K, 65 K) measurements have been used to determine the % freely accessible vs restricted mesoporosity in mesoporous Y zeolites (Figure 1, right).
(5) *Hysteresis scanning* to elucidate pore connectivity and pore desorption mechanisms and confirmed the presence of cavitation in Figure 1, right.

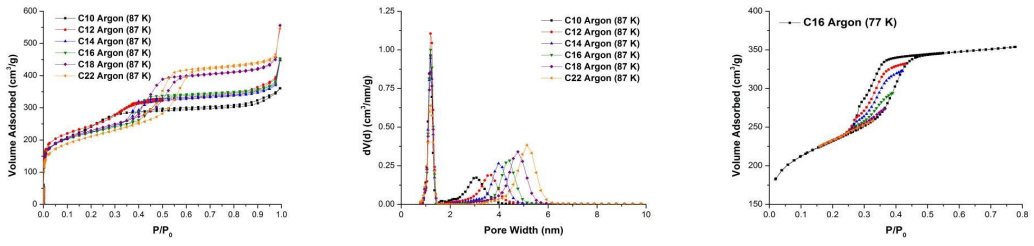

Figure 1. Argon (87 K) adsorption isotherms of a series of mesostructured zeolite Y (left), NLDFT pore size distributions from the argon (87 K) isotherms (middle), and hysteresis scanning curves on the argon (77 K) isotherm for one material (right).

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Probing the possibility of cooperativity of two divalent cations in Si-rich zeolites by Zn(II) emission quenching

E. Tabor*, J. E. Olszowka, P. Kubat, J. Dedecek

J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 3, Prague, Czech Republic

**edyta.tabor@jh-inst.cas.cz*

Keywords: binuclear sites, luminescence, ferrierite, Co(II) ions, Zn(II) ions

Introduction.

Distant binuclear transition metal (TM) ion sites stabilized in the zeolite matrix represent a new, recently discovered type of redox sites. [1] These sites are formed by two bare M(II) ions capable of the M(II)↔ M(IV) redox cycle, located in two opposite extra-framework cationic sites at a distance of. 7.5 Å. The distance between cations is short enough to allow them to perform the four-electron redox process, which can result in the splitting of two- or three-atom molecules, as was demonstrated for N_2O and O_2. Particularly facilitated splitting of O_2 is a significant step ahead in oxidation catalysis, as by this process a pair of highly active, so-called α-oxygens is formed. These α-oxygens are so active that they are able to oxidize methane at room temperature [1]. Moreover, the oxidation products formed are released without aid on effluent to the gas phase also at room temperature. However, the formation of distant binuclear TM ion sites in zeolites was up to now only predicted by DFT [2] and confirmed indirectly, by the activity of M(II)-ferrierite in the oxidation of methane at low temperature. Therefore, in this work, the introduction of Zn(II) (emitter) and Co(II) (quencher) to develop the method for studying the intrinsic property of the chosen FER matrix with Al distribution assuring the formation of binuclear catalytic centres with appropriate geometry is presented.

Experimental/methodology.

The formation of distant binuclear site formed by Zn(II) and Co(II) ions is evidenced by employing the time-resolved laser-induced emission spectroscopy of Zn(II) ions in the presence of Co(II) ions in ZnCo-ferrierite. Commercially supplied ferrierite (FER) with Si/Al 8.5, Tosoh Corporation Japan was employed for the preparation of ZnCo-ferrierite samples with various Zn and Co loadings. Co(II) ions were characterized by UV-Vis DR spectroscopy of dehydrated samples using Perkin–Elmer Vis spectrometer Lambda 19 equipped with an integrating sphere. Zn(II) ions were characterized using LKS 20 laser kinetic spectrometer (Applied Photophysics) excited by Lambda Physik COMPEX 102 excimer laser (wavelength 308 nm).

Results and discussion.

As it was reported previously, bare Zn(II) ions stabilized in extra-framework cationic sites of ferrierite exhibit luminescence with a lifetime varying from 50 to 130 μs in the dependence on the site accommodating Zn(II) ion. In the case of the presence of Co(II) co-cation in the ferrierite matrix, the Zn(II) luminescence lifetime is significantly shortened to only 6 – 11 μs. This indicates quenching of the Zn(II) luminescence by the neighbouring Co(II) ions *via* resonant energy transfer, analogously as it was already reported for Cu(I) ions in Al-rich zeolites.[3]

Acknowledgements

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Assessment of Ag-sites speciation in ZSM-5 zeolite - *operando* UV-Vis and FT-IR studies

K. Tarach[1], A. Kordek[1], K. Gora-Marek[1], M. Smoliło-Utrata[1], J. Martínez Triguero[2], F. Rey[2]
[1]*Faculty of Chemistry, Jagiellonian University in Kraków, Gronostajowa 2, 30-387 Krakow, Poland*
[2]*Instituto de Tecnología Química, Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas (UPV-CSIC), Avda. de los Naranjos s/n, 46022 Valencia, Spain*
*karolina.tarach@uj.edu.pl

Introduction. Silver ions incorporated to zeolite can serve as active sites in numerous catalytic reactions as the aromatization of alkanes, alkenes and methanol [1]. The reduction process of Ag^+ cations to various forms of Ag^0, clusters or nanoparticles, can occur upon the thermal treatment with CO, alcohols and alkylobenzenes [2]. Further, the thermal treatment itself plays an important role in the control of Ag species nature in zeolites. An isolated Ag^+ cations are the most favored at temperatures below 400 °C while higher temperatures facilitate their aggregation [3].

Experimental. The evolution of Ag species in the oxidative and reductive atmosphere was tracked in operando UV-vis studies. The temperature was increased gradually from RT to 500 °C with rate of 10 °C/min. The status of silver sites in zeolites will influence the process of catalytic oligomerization of ethylene and methane activation because of the Ag^+ cation itself can serve as the reaction site. Further, the activity of protonic sites present in reduced sample can be moderated by charged silver cluster presence. This aspect of the oligomerization activity influenced by the co-presence of Ag^+ cations was studied by means of 2D COS FT-IR spectroscopy of ethylene transformation over Ag-ZSM-5 at 375 °C over 10 h.

Results and discussion. It is well known fact that during oxidation at elevated temperatures the reduction of Ag^+ to Ag^0 can take place even in pure oxygen atmosphere. This is the case as the bands placed at 220-250 and 280 nm (Ag_m^+ and Ag_n^+ clusters, where m<n<8) increased significantly upon the thermal treatment in synthetic air flow from RT to 500 °C (Fig. 1). On the hand, under H_2 atmosphere with gradual increase of temperature to 500 °C leads to the formation of new kind Ag_x^+ with lower atomicity degree (4<x<8, 310 and 320 nm) accompanied by development of Ag_{NPs} (360 nm) (Fig.1B). The AgZSM-5 zeolite during ethylene oligomerization process is selective to the aromatic compounds, e.g. 1,2,4-trimethylbenzene (1505 cm^{-1}) and bulky aromatics seen as 1590 and 1570 cm^{-1} bands. Homogenous nature of the oligomerization products is reflected in the maps as well-resolved high intensity correlation peaks.

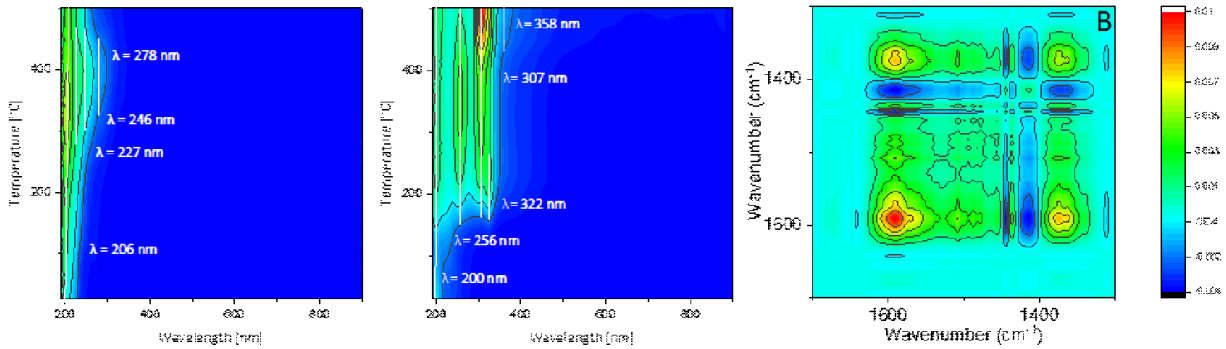

Figure 1 UV-vis spectra of Ag-ZSM-5 zeolite upon thermal treatment in oxidative (right) and reductive (middle) atmosphere, 2D COS maps of FT-IR spectra registered during ethylene oligomerizaiton over AgZSM-5 (left).

Acknowledgments
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Comprehesive assement of coke nature formed during ethylene oligomerization - influence of structural, textural and acidic parameters

K. Tarach[1], O. Rogala[1], M.Smoliło-Utrata[1], J. Martínez-Triguero[2], F. Rey[2], , K.Góra-Marek[1]

[1]*Faculty of Chemistry, Jagiellonian University in Kraków, Gronostajowa 2, 30-387 Krakow, Poland*
[2]*Instituto de Tecnología Química, Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas (UPV-CSIC), Avda. de los Naranjos s/n, 46022 Valencia, Spain*
*karolina.tarach@uj.edu.pl

Introduction. The nature of carbonaceous deposits is a crucial issue in catalytic reactions involving hydrocarbons transformations. The carbonaceous species plug the zeolite micropores and inhibit the diffusion of reactants and products. Prior knowledge regarding the paths of catalyst deactivation by means of carbonaceous moiety formation is unequivocally important for designing the zeolitic catalysts with targeted performance. In this respect, defining the relationship between the coke speciation and zeolitic catalysts properties which determines the carbonaceous deposit formation is important research goal.
Experimental. Carbonaceous species over the catalysts with acidic property are rapidly formed during the transformation of ethylene into higher hydrocarbons (ZSM-5, CBV2314E, Zeolyst, 325 °C, 5000 ml/(g·h), 15 hours). The thermoprogrammed oxidation experiments supported by mass spectrometry during coke removal from spent catalysts were performed from 200 to 550 °C in flow of synthetic air and additionally the FT-IR and UV-vis spectra were recorded. For quantitative analysis the TG experiments of total coke removal were perfomed. The qualitative analysis was further supported by GC-MS analysis of coke extracted from catalyst (dissolved in HF and extracted with CH_2Cl_2).
Results and discussion. The complex IR band around 1640-1550 cm^{-1} identifies the coke species formed during the oligomerization of ethylene over a series of ZSM-5. The position of the coke bands are indicative of its nature itself. Thus the bands centered at 1615 and 1575 cm^{-1} suggest are indicative for species formed by condensation reactions producing $C_6H_7^+$ olefinic cations (CH_2=CH−CH]CH=CH]CH^+ or cyclic alkenyl carbenium ions $C_6H_9^+$ - the 1575 cm^{-1} band) and polymethyl-benzenes as coke forming compounds (e.g. 1,2,4-trimethylbenzene, 1,2,3-trimethyl-benzene – the 1615 cm^{-1} band). The shape of the UV−vis spectra provides information that coke on spent catalyst consists of 1-, 2-, and 3-ring aromatic compounds that are identified by the bands appearing at 220 and 260 nm only. Both neutral and charged aromatics species are identified by a complex band in the 220-620 nm region. More specifically, a complex band at 425 nm is ascribed to 1-methylnaphthalene, in line with its relatively small bandwidth indicative of a narrow distribution of hydrocarbon species contributing to this band. The highest amounts of CO_2 are formed by the oxidation of residues in ZSM-5 zeolite at temperatures as high as 500 and 550 °C. This confirms further the aromatic character of coke species formed during ethylene oligomerization.

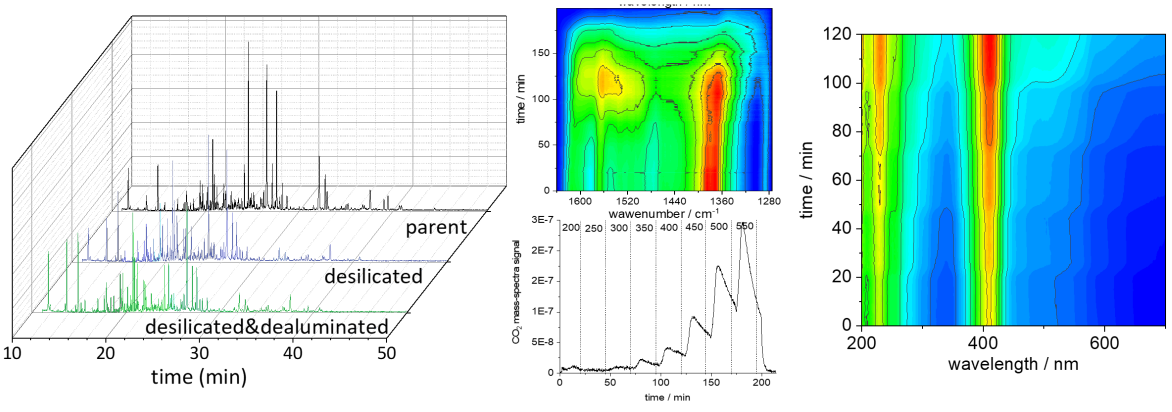

Figure 1. GC-MS results of coke analsysis (right), IR-MS (middle) and UV-vis (left) results of coke burnign-off

Acknowledgments

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Three-dimensional electron microscopy characterisation of silver before and after oxidation of CO, H_2 and CH_3OH

T. Bergh[1*], Y. van Valen[1], T. Skrzydlo[1], J. Yang[1], O.H. Bjørkedal[2], T. By[3], H.J. Venvik[1]

[1] *Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway.*
[2] *Dynea AS, Lillestrøm, Norway.*
[3] *KA Rasmussen AS, Hamar, Norway.*
[*] *tina.bergh@ntnu.no*

Keywords: silver, oxidation, surface morphology, focused ion beam, electron microscopy, tomography

Introduction. Silver is an effective catalyst in the partial oxidation of methanol, and silver particles are used industrially to produce formaldehyde. During interactions with oxygen at high temperatures (≳600 °C), the silver morphology changes drastically following oxygen dissolution and diffusion into silver and subsequent surface reconstruction and pore formation [1]. This restructuring is coupled with questions that have yet to be fully answered, including i) the role of hydrogen and carbon, ii) direct observations of the atomic planes in relation to the surface and pore facets, and iii) how the post-reaction morphology relates to the reaction dynamics. In this study, electron microscopy is employed to characterise annular silver catalysts before and after oxidation in various reaction atmospheres, with the main goal of disclosing the (sub-)surface morphological and microstructural changes occurring in three dimensions.

Experimental/methodology. An annular reactor [2] is used with hollow cylindrical silver catalysts (⌀ 10 mm) that are heated in steps up to 700 °C and subsequently cooled. Several samples are studied, including as-received silver (A), silver heated in N_2 (B), and silver after oxidation of CO (C), H_2 (D), CO and H_2 (E), CH_3OH (F) and CH_3OH and H_2O (G). Scanning and transmission electron microscopy (SEM and TEM) techniques are applied to characterise the pores and facets. Focused ion beam (FIB)-SEM is used to obtain three-dimensional tomographic reconstructions [3] of the (sub-)surface region. The grain structure is revealed by electron backscatter diffraction and scanning precession electron diffraction (SPED) [4].

Results and discussion. The as-received silver (A) shows small grains and pores within the near surface region (≲1 µm), but no surface facetting. The heated samples display facets mainly corresponding to {111} planes, and the grain structure indicates recrystallisation and twinning. The FIB-SEM tomography discloses smaller rounded (∽10 nm) and larger often facetted pores (∽1 µm). Figure 1 shows selected results from silver after CO oxidation (C). Similarities and differences between the catalysts are shown and discussed.

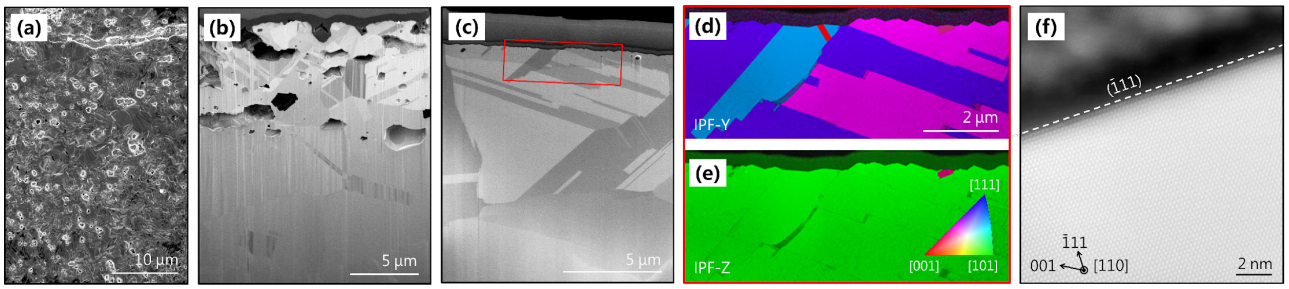

Figure 1: Silver after CO oxidation (C). SEM images showing (a) top-view, and (b) and (c) cross-sections milled by FIB. (d) and (e) orientation maps obtained from SPED data. (f) high angle annular dark field STEM image.

Acknowledgments

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Electrified ethylene epoxidation using computationally predicted catalytic formulation

M. Huš[1,2], J. Teržan[1,3,*], A. Sedminek[3], S. Gyergyek[3], M. Grilc[1], B. Likozar[1], A. Hellman[2]

[1]*National Institute of Chemistry, Department of Catalysis and Chemical Reaction Engineering, Hajdrihova 19, SI-1001 Ljubljana, Slovenia*

[2]*Chalmers University of Technology, Department of Physics, Fysikgränd 3, SE-41296 Göteborg, Sweden*

[3]*Department of Synthesis of Materials, Jožef Stefan Institute, Jamova Cesta 39, 1000 Ljubljana, Slovenia*

*e-mail: janvit.terzan@ki.si

Keywords: sustainability, decarbonisation, electrification, climate neutrality

Introduction. Ethylene epoxidation is an essential selective oxidation process in the industrial production of materials such as glycols, ethers, ethanolamines, and ethoxylates. The process involves the conversion of ethylene to ethylene epoxide (EO) using doped silver catalysts. The silver is doped with various elements, such as antimony, bismuth, caesium, chlorine, copper, or noble metals, to improve selectivity. Despite the effectiveness of silver as a catalyst, there is ongoing debate about the microscopic origins of the beneficial effects of dopants.

Experimental/methodology. In this study we synthesized, screened, and characterized catalysts predicted by computational screening to better understand the reaction mechanism, predict more effective catalysts, and explain the favourable effects of known dopants. The formulations were predicted by the use density functional theory (DFT) calculations to examine the reaction mechanism on nine late-transition metals. They then use scaling relations and the Brønsted–Evans–Polanyi (BEP) relations to identify correlations between calculated reaction parameters and a unique descriptor for each catalyst. This screening predicts high-performing alloys, such as silver with copper, cadmium, zinc, and thallium, and provides a framework for future research. The synthesized materials were characterized by XRD, TEM, XPS, and pulse chemisorption of oxygen. Finally, the materials were analysed for their capacity to selectively oxidize ethylene to ethylene oxide in a custom electrified reactor.

Results and discussion. The experimental results show that all tested catalysts produced ethylene oxide (EtO), but with CO2 as the majority product. Adding small amounts of Cu to a silver-based catalyst increases EtO selectivity by over 50% (Figure 3). The highest activity and EtO selectivity was found in the Pb and Cu modified catalyst, outperformed by the Cd modified tri-metallic catalyst. The In and Zn modified tri-metallic catalysts were not efficient for ethylene epoxidation. XRD analysis showed that adding metals to silver does not affect the average particle diameter of the catalysts. Pulse oxygen chemisorption showed that adding metals to silver increases oxygen coverage, with a limit before it causes total oxidation of EtO to CO2 and H2O. TEM analysis revealed that the Ag catalyst particles consist of large alumina flakes decorated with Ag nanoparticles.

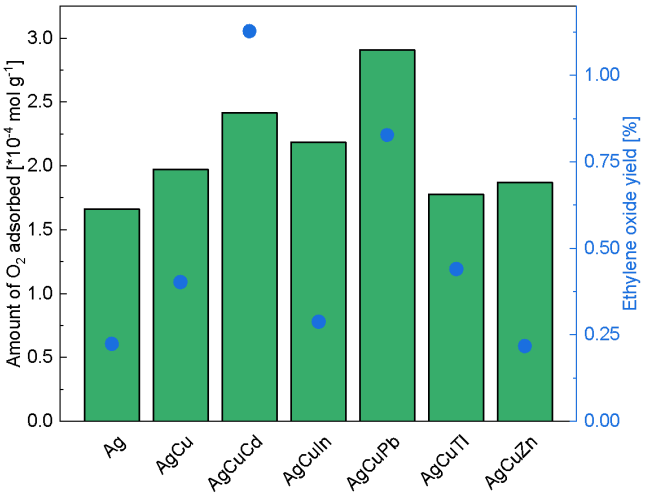

Figure SEQ Figure * ARABIC 1: The graphs shows the normalized adsorption of O_2. It is overlaid with the yield in selective oxidation of ethylene.

Combining spectroscopic online monitoring with additive manufacturing in continuous flow liquid phase processes

V. Truttmann[1], M. Kaya[2], C. Klahn[3], B. Häfner[4], C. Jakob[4], D. Doronkin[1,5], E. Saraçi[1,5], J.-D. Grunwaldt[1,5,*]

[1]*Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany*
[2]*Institute for Micro Process Engineering, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany*
[3]*Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe, Germany*
[4]*Evonik Operations GmbH, Hanau-Wolfgang, Germany*
[5]*Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany*
**vera.truttmann@kit.edu*; *grunwaldt@kit.edu*

Introduction. Liquid phase continuous flow synthesis has become an important tool towards a more sustainable production of fine chemicals, often showing better performance and being less hazardous than classical batch processes.[1] Furthermore, improved process control is possible by using spectroscopic online monitoring.[1-3] Typically, spectroscopic probes or flow cells are placed after the respective flow reactor and thus, the data at the point of measurement do not fully represent the actual reaction taking place in the reactor. This not only complicates thorough reaction mechanism studies, but also the establishment of a real-time control loop to achieve reliable process control for increased efficiency.

These problems can be overcome by use of additive manufacturing (AM), which can generate advanced reactor geometries significantly improving e.g. mixing of reactants or heat transfer.[4] Additionally, the versatile features of AM enable the design of tailored solutions for the integration of spectroscopy into a continuous flow (micro)reactor.

Experimental/methodology/discussion. A continuous flow set-up including a customized stainless steel 3D-printed reactor was developed in-house and tested for an organometallic model reaction (Grignard reaction). Its performance regarding yield, selectivity, but also temperature management is compared to both a classical batch process as well as a standard continuous flow set-up without additively manufactured parts. Furthermore, online ATR-IR spectroscopic monitoring is implemented, first after the flow reactor and then inside the AM-reactor, and outcomes are compared. Finally, while focused mainly on mid-infrared spectroscopy, also other spectroscopic techniques (e.g. NIR) are evaluated to identify the optimal method in terms of safety aspects, chemical suitability and economic considerations.

With this case study we aim to demonstrate that combining novel manufacturing techniques with advanced *in situ/operando* spectroscopy has the potential to facilitate investigation and understanding of (catalytic) reaction mechanisms as well as to improve process control and automation. These insights provide significant benefits for both academic purposes as well as for industrial applications.

Acknowledgments
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Mössbauer Spectroscopy Study into Promoter Effects in Fe-Based Water-Gas Shift Catalysts

L.G.A. van de Water,[1*] M.I. Ariëns,[2,3] A.I. Dugulan,[2] E. Brück,[2] E.J.M. Hensen[3]

[1]*Johnson Matthey, Billingham, Cleveland, TS23 1LB, United Kingdom*
[2]*Delft University of Technology, 2629 JB, Delft, The Netherlands*
[3]*Eindhoven University of Technology, 5600 MB, Eindhoven, The Netherlands*
[*]*Leon.vandeWater@matthey.com*

Introduction

Fe-based mixed oxide catalysts have been used for over a century to catalyse the high-temperature water-gas shift (HTS) reaction to produce hydrogen from fossil or renewable sources. In this work, Mössbauer spectroscopy (MB) was used to study the incorporation mechanism of the Cr and Cu promoters, which are known to increase catalyst stability and activity of Fe-based HTS catalysts, respectively. MB is a powerful tool to investigate the electronic structure, bonding properties and magnetic behaviour of materials containing nuclei that display the Mössbauer effect, of which ^{57}Fe is by far the most widely studied.[1] Small changes in MB hyperfine interactions provide insight into the extent and manner of Cr and Cu incorporation into the calcined precursors and the reduced active catalyst phases. Catalyst performance under industrially relevant HTS conditions of a range of catalysts containing alternative promoters to Cr was studied and combined with results from MB spectroscopy to derive structure-performance relations.

Experimental/methodology

A range of Fe-Cr, Fe-Cr-Cu and Fe-M(-Cu) mixed oxides (M = Al, Ga, In, Mn, Zn, Nb) was prepared by co-precipitation followed by calcination. The Fe^{3+} catalyst precursors were subjected to industrially relevant HTS conditions (450 °C, 25 bar) for four days. The aged catalysts were analysed by MB, XRD and XPS after reaction.

Results and discussion

Small changes in the MB hyperfine interactions revealed that both Cr and Cu are incorporated into the fully oxidised Fe-Cr-Cu catalyst precursor. Upon reduction to the active magnetite phase, Cu is expelled from the mixed oxide lattice whilst Cr is fully incorporated into octahedral sites of the spinel structure, even at the maximum promoter level of 12 at%.[2][3] Substitution of Cr with alternative promoters results in a range of substitution patterns: Al and Zn substitute both tetrahedral and octahdral Fe ions, whilst Ga and Mn exclusively occupy octahedral sites. In and Nb are initially present at octahedral sites; however, these large cations do not remain in the lattice and are expelled from the structure under reaction conditions. Of the alternative promoters, Al displayed highest activity and stability under the applied testing conditions.[4]

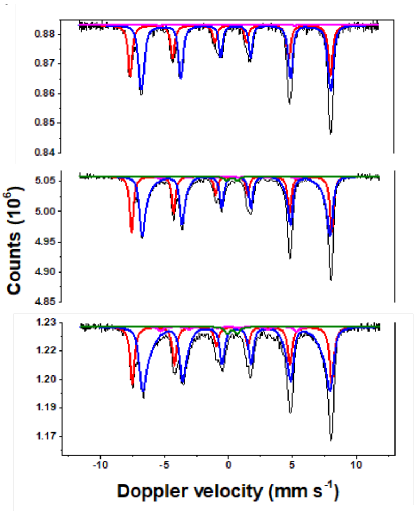

Figure 1. MB spectra of Fe_3O_4 and $Fe(Cr)_3O_4$.

Acknowledgments

The project "Application of advanced combined in situ Mössbauer/IR/GC characterisation under industrially relevant conditions to underpin and accelerate development of improved Fe-based catalysts", project number 731.015.419 of the research programme LIFT, has received funding from the Dutch Research Council (NWO) and Johnson Matthey.

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Effect of the impregnation method on the properties of sulfided NiMo hydrotreating catalysts

J. Kattelus[1], J.A. Velasco[1*], P. Auvinen[1], A. Singh[1], A. Arandia[1], K. Meinander[1], H. Jiang[1], S. Albersberger[2], R. Karinen[1], R.L. Puurunen[1]

[1]*Aalto University, Dept. of Chemical and Metallurgical Engineering, Kemistintie 1, 02150 Espoo, Finland*
[2]*Neste Oyj, Jalostamontie 36, 06850 Porvoo, Finland*
[*]*jorge.velasco@aalto.fi*

Keywords: hydrodenitrogenation, sulfide NiMo catalyst , impregnation, citric acid

Introduction. The future of fuel supply involve the utilization of feedstock materials from conventional and nonconventional sources and the selective removal of sulfur, oxygen and nitrogen is among the most critical and challenging aspects of the upgrading [1]. Hydrodenitrogenation (HDN) becomes particularly challenging for processing biobased feedstocks since they comprise different nitrogen containing compounds than fossil-based feedstocks [2]. NiMo sulfide supported on alumina is traditionally used as catalyst for HDN [3] and it has been reported that the preparation method influences the properties of the resulting NiMo catalyst which in turn defines the hydrotreating activity [4]. Catalysts with short MoS_2 slabs length and large MoS_2 stack height resulted in an improved HDN activity [5]. In addition, it was found that the use of citric acid (CA) in the impregnation results in a relatively higher MoS_2 stacking number and facilitates the formation of the NiMoS phase [6]. However, the impregnation step at which citric acid is added might also play a role on the resulting catalyst properties [6]. In this work, we explore the effect of the impregnation method and the use of citric acid as additive on the physico-chemical properties of sulfided NiMo catalysts supported on γ-alumina. The impregnation methods studied in this work were wet co-impregnation, and incipient wetness with co- and sequential impregnation of Mo and Ni metal precursors.

Experimental. Ammonium heptamolybdate hexahydrate and nickel nitrate tetrahydrate were used as metal precursors for wet and incipient wetness impregnation. Citric acid (with a CA/Ni molar ratio of 1.6) was used optionally as an additive during impregnation. The impregnated supports were calcined at 500 °C for 2 h. Sulfidation of the calcined catalyst precursors was was carried out in batch conditions and it consisted of an initial drying with 10 bar N_2 at 180 °C for 1 h followed by sulfidation with 10 vol% H_2S/H_2 at 400 °C for 2 h. Characterization techniques included powder X-ray diffraction (XRD), inductively coupled optical emission spectroscopy (ICP-OES), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) combined with energy-dispersive X-ray spectroscopy (EDS), and Raman spectroscopy.

Results and discussion. Our results show that the use of citric acid during catalyst preparation resulted in a reduced amount of crystalline MoO_3 and higher metal loading in the calcined catalyst precursors. The formation of the HDN active NiMoS phase was confirmed in all prepared catalysts by XPS measurements. Additionally, TEM analysis of the sulfided catalysts revealed that the catalysts prepared with citric acid presented shorter MoS_2 slabs and a higher stacking number than those prepared without addition of citric acid. In general, comparing the different methods studied in this work, the addition of citric acid during the impregnation steps resulted in catalysts with enhanced physico-chemical properties which can be beneficial for HDN reactions [5, 6].

Acknowledgments
This work was financially supported by Neste Oyj (Neste-Aalto HDN Cat project). E. Verkama is thanked for fruitful discussions on catalyst preparation and characterization, and H. Revitzer for some of the ICP-OES analyses.

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Exclusive Effect Of Two-Dimensional Supports On Platinum Nanocatalyst Properties

M. Veselý[1*], I. Danylo[1], L. Koláčný[1], S. Rimpelová[2], M. Pitínová[1], T. Hartman[3], Z. Sofer[3]

[1]*University of Chemistry and Technology Prague, Department of Organic Technology, Technická 5, 166 28, Prague, Czech Republic;*
[2]*University of Chemistry and Technology Prague, Department of Biochemistry and Microbiology, Technická 3, 166 28, Prague, Czech Republic;*
[3]*University of Chemistry and Technology Prague, Department of Inorganic Chemistry, Technická 5, 166 28, Prague, Czech Republic;*
[*]*veselyr@vscht.cz*

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Introduction. The text should be 11-point Calibri.
Experimental/methodology. The text should be 11-point Calibri.
Results and discussion. The text should be 11-point Calibri. Figures and tables can be embedded in this section. Caption (Calibri, 10 pt., Bold) should be given below the figures & above the tables.

Acknowledgments
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References
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[1] Makadia, H.K.; Siegel, S.J. *Polymers* **2011**, *3*, 1377-1397.
[2] Siqueira, G. et al. *Polymers* **2010**, *2*, 728-765.

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e text should be in the single-column format in A4 paper with margins 2cm on all sides.
The maximum length of the abstract is one page A4.
The file must be saved in the format MS Office Word (doc, docx, **NOT pdf**).
The name of presenting author should be underlined.

A combined XAS-TRM approach for the kinetic analysis of the Standard SCR redox mechanism over Cu-CHA catalysts

R. Villamaina[2], M. Ruggeri[2], H. Islam[2], F. Gramigni[1], U. Iacobone[1], N. Usberti[1] , N. Nasello[1], I. Nova[1], L. Mantarosie[2] , J. Collier[2] , M. Amboage[3], E. Tronconi[1*]

[1]*Laboratory of Catalysis and Catalytic Process, Dip. Di Energia, Politecnico di Milano, Italy*
[2]*Emission Control Department, Johnson Matthet Technology Centre, UK*
[3]*Diamong Light Source, UK*
[*]*enrico.tronconi@polimi.it*

Keywords: Cu-CHA, SCR redox cycle, XAS, TRM, Emission control, NH_3-SCR

Introduction.

The NH_3 Selective Catalytic Reduction (NH_3-SCR) is currently considered the leading technology for NO_x abatement from Diesel engines [1-3]. In literature, there is a wide consensus about the redox nature of the Standard SCR chemistry. However, the detailed scheme of the full SCR redox cycle is still debated [3]. In this work, we investigate kinetic features involved in the RHC and OHC of the SCR redox cycle using both Time Resolved X-ray Absorption spectroscopy (XAS) as well as simple Transient Response Methods (TRM).

Experimental/methodology.

Kinetic investigations were carried out on 1.7% and 2.1% w/w Cu-CHA (SAR25) model catalyst samples (powders) provided by Johnson Matthey. XAS measurements were performed in a quartz capillary reactor (GHSV = 136500 $cm^3/h/g_{cat}$ (STP)) on the energy dispersive branch of beamline I20 at Diamond Light Source, Didcot, UK. XAS spectra were then analyzed by Multivariate Curve Resolution. TRM experiments were performed in a quartz micro-reactor (GHSV = 450000 $cm^3/h/g_{cat}$ (STP)) and the temporal evolution of the gas phase was monitored by FTR+MS analyzers at Politecnico di Milano. The TRM Cu^{II} reduction data were then fitted according to the transient integral model of the test flow reactor discussed in [4].

Results and discussion.

XAS profiles representative of the Cu oxidation state were used to verify the kinetics independently developed over Cu-CHA by gas phase transient response methods. Figure 1a shows that the evolution of Cu^{II} and Cu^{I} ions measured by XAS experiments during the NO+NH_3 reduction pulses was well predicted using the same RHC kinetics (2nd order in Cu^{II}) that successfully fitted the NO+NH_3 TRM experiments. The equivalence of the two techniques further validates a quadratic dependency on Cu^{II} for the reduction half cycle, consistent with a dual site mechanism. The opposite was done in the case of the OHC: transient response experiments were used to further investigate aspects related to the re-oxidation in NO+O_2 and O_2 only. Combining the two techniques has highlighted that NO is not involved in the re-oxidation of Cu sites. O_2 can re-oxidize Cu sites leaving them solvated with NH_3. NO presence leads instead to a more complex behaviour and consumption of ammonia prior complete oxidation (Figure 1b,c).

A strong synergy between the two complementary techniques exists: they can be used equivalently to investigate the RHC, but their use in combination has unveiled important mechanistic aspects of the OHC.

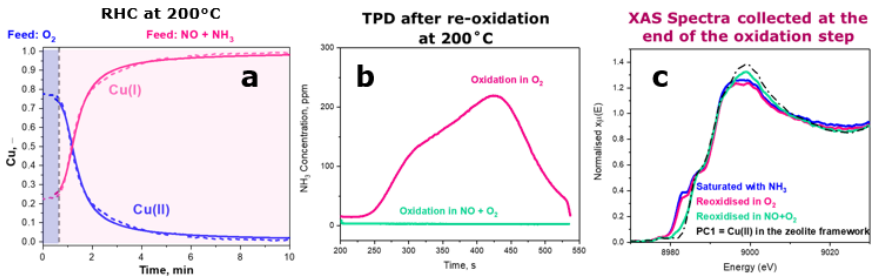

Figure 1 a) RHC: experimental data (EDE runs) versus kinetic simulations; b) NH_3 TPD performed after reoxidation in O_2 or NO + O_2; c) XAS spectra collected at the end of the oxidation step in O_2 vs NO+O_2.

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Operando Luminescence Thermometry of Propane Dehydrogenation Catalysis

R. Vogel[1*], Freddy T. Rabouw[1], Bert M. Weckhuysen[1]

[1]Inorganic Chemistry and Catalysis, Department of Chemistry, Utrecht University, *Utrecht, The Netherlands*
[*]*r.vogel@uu.nl*

Keywords: Propane dehydrogenation, luminescence thermometry, in-situ spectroscopy

Introduction

Catalytic propane dehydrogenation (PDH) is an industrial route towards the production of propylene. Unfortunately, the formation of carbon deposits (coke) on the catalyst material, results in gradual activity loss. Catalytic performance, including activity and selectivity, is often regained in an oxidative regeneration step.[1] In the processes of catalysis and catalyst regeneration, local temperature is expected to influence events on the catalyst surface that affect its overall performance and long-term stability. Figure 1a illustrates how the endothermic dehydrogenation process over a Pt-Sn/Al_2O_3 PDH catalyst can result in a locally lower temperature at the catalyst while the exothermic regeneration process can result in strongly increased local temperatures. Potentially, information on the local temperature can be used to adjust the regeneration procedure in order to reduce catalyst degradation. In this work, we have developed a non-invasive thermometry technique based on the temperature-dependent luminescence of Eu^{3+} to gain insight in the local temperature of the catalyst during PDH and regeneration.

Methodology

Figure 1b shows that Eu^{3+} can serve as a temperature sensor. The luminescence originating from two thermally coupled energy levels, $^5D_1$ and $^5D_1$ changes as a function of temperature.[2] Spectra recorded at a known temperature can be used as a reference to deduce the temperature of a sample containing Eu^{3+} at an unknown temperature.

Results and discussion

Figure 1c reveals a strong exothermic effect during the regeneration of a coked Pt-Sn/Al_2O_3 PDH catalyst. The catalyst was mixed with the temperature sensor and heated in an O_2-containing atmosphere. Time-resolved Eu^{3+} emission spectra revealed a fast local temperature rise after the reactor temperature reached 450°C. This observation can be coupled to the combustion of carbon deposits and the regeneration of the catalyst. Combining local temperature information with thermogravimetric analysis and in-situ spectroscopy techniques, such as UV-Vis and Raman spectroscopy, builds a complete picture of the processes occurring on the surface during regeneration.

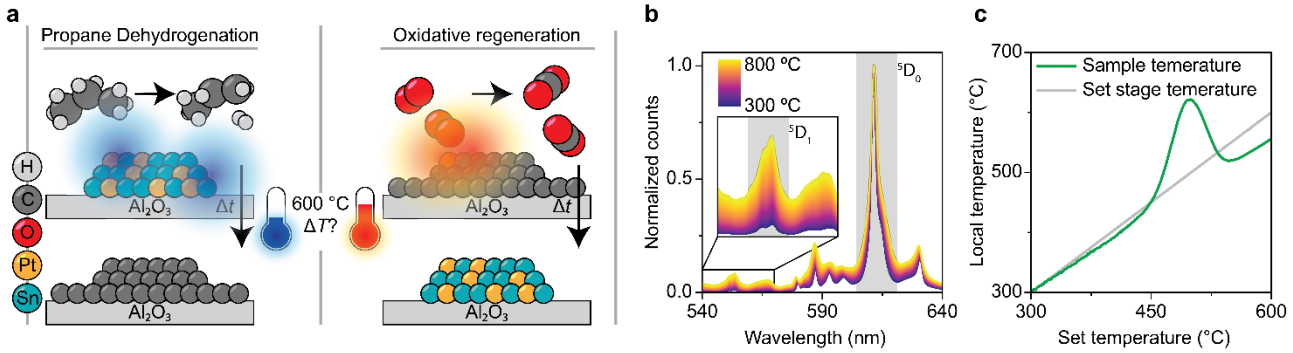

Figure 1 – (a) Endothermic and exothermic effects during propane dehydrogenation (PDH) and oxidative regeneration over a Pt-Sn/Al_2O_3 catalyst; (b) Normalized Eu^{3+} emission spectra between 300 and 800°C. (c) Local temperature during regeneration of a coked PDH catalyst.

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Grazing incidence studies of thin film Pd-ZnO/SiO2 catalysts for C_2H_2 hydrogenation

Urvashi Vyas[1],[2], [3], Andrew M. Beale[1],[2], Francesco Carla[3], Katarzyna Skorupska[4], Matus Stredansky[4], Eylül Öztuna[4], Alexander Steigert[5], Simone Raoux[6]

[1] *Department of Chemistry, UCL, 20 Gordon Street, WC1H 0AJ, London, UK*

[2] *Research Complex at Harwell, RAL, Harwell, Didcot, OX11 0FA, UK*

[3] *Diamond Light Source, RAL, Harwell, Didcot, OX11 0FA, UK*

[4] *Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany*

[5] *Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institute Nanospectroscopy*

[6] *Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institute Nanospectroscopy, Department of Physics, Humboldt University of Berlin*

urvashi.vyas.19@ucl.ac.uk

Keywords: Catalysis, *in situ*, *Operando*, X-Ray Reflectivity, Grazing Incidence X-Ray Diffraction, Thin-films

Introduction: *Operando* Grazing Incidence X-ray Diffraction (GIXD) and X-Ray Reflectivity (XRR) were applied under *in situ* conditions to study 2D model catalysts during activation in H_2 and acetylene hydrogenation (C_2H_2 + H_2). These methods were combined with online mass spectrometry (MS) analysis to determine the relationship between structure and activity. Model 2D catalysts comprised of Pd (mean thickness ~10 nm) and 36 nm of ZnO deposited on single crystal SiO_2/Si(100) were studied. Reduction in 2% H_2 followed by acetylene hydrogenation was performed as a function of temperature (90 to 350 °C) and 1 barg in order to follow the structure evolution, particularly to determine the role of Pd speciation (Pd metal, PdC, PdH and β-PdZn with the support) on semi-hydrogenated (ethylene) and fully hydrogenated (ethane) product formation. This work also addressed the issue of the reversibility of the Pd-C species that is formed during reaction conditions. The results allowed us to obtain a unique insight into the structural transformations occurring at the metal-support interface and its implications on catalyst performance.

Experimental/methodology. The Pd/ZnO_SiO_2 samples were prepared at the Helmholtz-Zentrum (HZB) in Berlin as a part of the CatLab project. These samples comprise of Si and Si-200 nm SiO_2 substrates which have been sputter coated with Pd and ZnO respectively. In this experiment, samples with the following thickness have been used: 10 nm Pd and 36 nm ZnO layers. The Pd and ZnO is being sputtered on the substrate by DC-sputtering. The grazing incidence measurements were performed using an incident angle of 0.6199°. The detector images were processed to obtain a 2θ projection of the diffracted intensities. The sample was mounted on a stainless-steel plate using silver paste glue and placed inside a sealed reactor complete with an X-ray transparent Beryllium dome with K-type thermocouple attached on the sample plate near the sample. The reactor was connected to a gas delivery system comprising of switching valves and mass flow controllers which enabled complete control of gas mixing and flow rates.

Results and discussion. The ratio between H_2 & C_2H_2 impacts the catalytic activity. The pristine sample comprises crystalline Pd as evidenced by the presence of reflections at 15.88°° (111), 18.38°° (200), 26.02°° (220), 30.52°° (311) and 31.83°° (222). This is accompanied by ZnO reflections at 12.63°° (100) and 14.38°° (101). Reduction at 90 °C displays the same reflections as the initial reading but all at a lower intensity. From 1:1 (H_2:C_2H_2) at 90 °C onwards, there are only two phases present throughout the remaining data. The positions of these reflections do not change. The PdC phase is shown to form by the presence of reflections at 15.62°° (111), 18.03°° (200), 25.58°° (220), 30.08°° (311) and 31.48°° (222). The ZnO reflection positions remain & are unchanged. XRR data shows changes at the interface of the sample, with changes in roughness affecting the quality/shape of oscillations. The XRR shows the presence of Pd, ZnO and PdZn. The GIXD pattern does not show any presence of PdZn at this stage. It is likely the PdZn alloy formation is in its early stages, thus, the deeper probing from XRR has proven to be beneficial to see these physiochemical changes.

References

On the basicity dermination of thermally unstable materials

L. Dolejšová Sekerová[1], I. Paterová[1], E. Vyskočilová[1*]

[1]*Dpt. of organic technology, University of Chemistry and Technology Prague, Prague, Czech Republic*
[*]*eliska.vyskocilova@vscht.cz*

Keywords: basicity, sorption, HPLC/MS, UV/Vis, layered double hydroxides

Introduction. The basicity of materials designed as catalysts is one of the most important factors in evaluating catalytic activity. Typically, the basicity is determined using the TPD method [e.g., 1] of the preadsorbed gaseous acidic probe – CO_2 is used most often. However, this method needs thermal pretreatment of the measured samples necessary that is, of course, problematic for thermally labile samples. Moreover, the CO_2 probe is a small molecule that can access even the more hindered basic sites. Thus the results might be misrepresented for reactions with larger molecules as basic catalysts are often used for, e.g., aldol condensation reactions.

Experimental/methodology. Mixed Mg-Al oxides (MO) with different ratios Mg:Al (prepared by precipitation–calcination method) were used as model materials for development of new method for basicity evaluation. Two methods – UV/Vis and HPLC/MS - were used. Both methods used anthranilic acid as a probe molecule, and the results were compared with the results obtained by commonly used TPD of CO_2. The optimized procedure was applied to the basicity determination of thermally unstable layered double hydroxides (LDH) prepared from model mixed oxides. The basicity values were compared with the results of testing of catalytic activity in aldol condensation reactions [2,3].

Results and discussion. The probe molecule was applied from acetonitrile solution by wet sorption. Mixed oxides were calcined prior to the sorption. HPLC/MS served to determine the amount of basic sites. At the same time, UV/Vis confirmed that the probe molecule was attached to the surface by acid-basic interaction, and simple sorption was avoided. The dependence of UV/Vis absorption properties of anthranilic acid under different pH was measured. The significant shift of absorption band was detected in basic as same as an acidic solution. The amount of basic sites measured by HPLC/MS decreased in the row MO2 ≈ MO2.5 > MO3 > MO3.5 (the number was the ratio Mg:Al). The anthranilic acid adsorbed amount ranged from 18.5 to 7.5 mg/g of material. This row was the same as in the determination of the amount of basic acids sites by TPD CO_2. The more challenging was the basicity determination of LDHs, which we prepared by rehydration of the tested mixed oxides. Thus we prepared four LDHs denoted as LDH2, LDH2.5, LDH3, and LDH3.5 (the number corresponds to the ratio Mg:Al). LDHs adsorbed a significantly higher amount of the probe molecule as expected. The lowest adsorbed amount was 197.8 mg/g of material, which was ten times higher than the highest amount adsorbed in the case of MO. The basicity of LDHs materials decreased in the row LDH3.5 > LDH2.5 > LDH3 > LDH2. However, the catalytic activity of these materials differed. We have found out that the different textural properties of materials may explain the different behavior of materials after rehydration. As the catalytic activity measurement took only 6 hours while the basicity measurement was performed until the equilibrium was reached, the more precise comparison was the probe molecule's consumption rate. In such a case, the consumption rate decreased in the row LDH2.5 > LDH3.5 > LDH3 > LDH2, which followed the catalytic activity of the materials. We can conclude that we have developed a method for evaluating the basicity of solid materials that is also applicable to the thermally unstable materials of the layered double hydroxide type. This method offers a promising way of further characterization of basic materials.

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Perspectives for in situ/operando research at the SOLARIS synchrotron in Krakow

A. Wach[1*], A. Maximenko[1], G. Gazdowicz[1], K. Sowa[1], P. Korecki[1,2], M. Sliwa[1,4], A. Lewera[3], W. Macyk[4], J. Szlachetko[1], Z. Sojka[4]

[1]*SOLARIS National Synchrotron Radiation Centre, Jagiellonian University, Krakow, Poland*
[2]*Faculty of Physics, Astronomy and Applied Computer Science, Jagiellonian University, Krakow, Poland*
[3]*Biological and Chemical Sciences, Faculty of Chemistry, University of Warsaw, Warswow, Poland*
[4]*Faculty of Chemistry, Jagiellonian University, Krakow, Poland*
[*]*anna.wach@uj.edu.pl*

Keywords: X-ray spectroscopy, synchrotron, in situ, operando, catalysis

Introduction. The SOLARIS National Synchrotron Research Centre is a third-generation light source operating at medium electron energy since 2015 in Krakow, Poland. The storage ring operates at a final energy of 1.5 GeV in a decay mode with a maximum current of 500 mA and a total lifetime of 15 h. As the only synchrotron light source in central and eastern Europe, SOLARIS has the potential to become the leading applied research facility in the region. The presence of bending magnets and insertion devices within the storage ring allows to cover a wide spectrum of emitted photons from VUV to the hard X-ray region. Thanks to its unique properties and excellent parameters, SOLARIS provides different photon- and electron-based techniques for material investigation in various research fields, e.g. catalysis, material and surface science and environmental chemistry. Presently, the synchrotron experiments are possible at five beamlines (overall six end-stations) and a cryo-microscopes facility, while three additional beamlines are under construction and several more are in conceptual preparations.

Results and discussion. We will present current studies and future perspectives of in situ/operando project at SOLARIS. In particular, we will present the development of an operando endstation that will allow for synchrotron-based multitechnique studies (combinations of X-ray spectroscopy with complementary techniques) at hard x-ray energies. The endstation will be designed to be used at the two hard X-ray beamlines of SOLARIS, namely ASTRA and PolyX beamlines. The ASTRA beamline is designed for X-ray Absorption spectroscopy (XAS) measurements at tender and higher X-ray energies (from 1 to 15 keV). XAS is element specific, sensitive to the chemical environment of the absorbing atom and together with the high X-ray penetration depth of the X-rays used, uniquely suited for studying catalysts under relevant conditions (in situ/operando). The PolyX beamline is a compact bending magnet beamline in the hard X-ray energy range (4-15 keV). The beamline is based on polycapillary optics, which in conjunction with energy-dispersive X-ray absorption and emission spectroscopy and von Hamos spectrometer will enable time-resolved studies. Microfocus capabilities of the beamline are important for in situ experiments where a local X-ray probe is essential for precise determination of the sample's chemical state.

Further, we will describe the parallel development of the second endstation dedicated to NAP-XPS studies. NAP XPS allows for in situ investigations of catalysts in gaseous environments in the mbar pressure range. These near ambient pressure XPS, have opened up new opportunities to study dynamic modifications at surfaces and correlate them with the catalytic performance. We will discuss the possibility to conduct research with NAP-XPS beamline in soft X-ray energy range, which will be an ideal operando measurement method for investigating the electronic structures of materials at gas/solid interfaces, with simultaneous monitoring of material function.

Acknowledgments
This work was partially supported by the National Science Centre (Poland) under grant number 2020/37/B/ST3/00555.

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Bulk chemicals and polymers

Kinetic Coupling of Ethane and CO_2 Activation on Metal Oxide Catalysts

Rui Yao,[1] Guangming Cai,[1] Jayson Pinals,[2] Roham Dorakhan,[1] José E. Herrera,[3] Prashant Deshlahra,[2] and Ya-Huei (Cathy) Chin[1]*

[1] *Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Canada;* [2] *Department of Chemical and Biological Engineering, Tufts University, Medford, Massachusetts, USA;* [3]*Department of Chemical and Biochemical Engineering, Western University, London, Canada.*

*cathy.chin@utoronto.ca

Keywords: Metal oxides, C-H activation, CO_2, molybdenum oxide, alkane, oxidative dehydrogenation

Introduction. Activation of C-H bond in alkanes and C=O bond in CO_2 on transition metal oxides is of industrially importance in shale gas conversion, commodity chemical production, and/or in CO_2 utilization. Through kinetic assessments, UV-vis and XPS spectroscopic studies, and density functional theory calculations, we establish the common mechanistic traits and active site requirements for these reactions—when analyzing them at the molecular scale level, the reactions contain several kinetically coupled catalytic cycles that involve the activation of the reductant on metal cation-oxygen anion site pairs and the activation of oxidant on oxide surfaces.

Experimental/methodology. Molybdenum catalysts promoted with Co, Fe, and Ni were prepared by wet impregnation methods. Kinetic assessments of alkane-CO_2 turnovers were carried out in a microcatalytic fixed bed reactor. UV-vis and XPS spectroscopies were carried out either in-situ or transferred from reactor under controlled environments. Density functional theory calculations were performed using VASP.

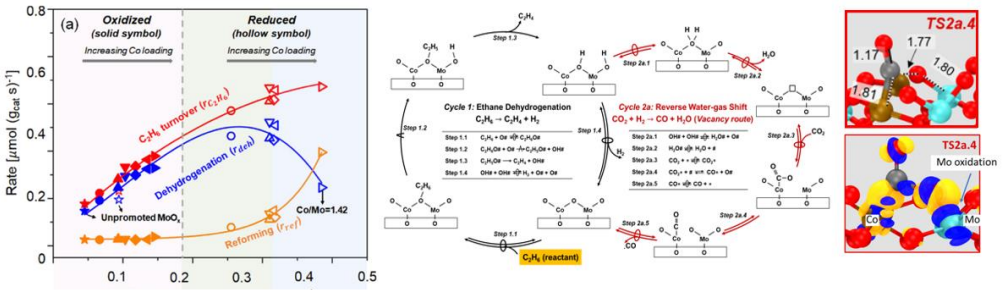

Figure 1. (a) Rates (per mass) of total C_2H_6 turnover (r_{C2H6}), dehydrogenation (r_{deh}), and reforming (r_{ref}) versus the RWGS rates (r_{RWGS}), after C_2H6–CO_2 catalysis (5 kPa C_2H_6, 10 kPa CO_2, 6000 cm^3 g_{cat}^{-1}) for 15 h at 873 K on a series of CoO−MoO_x catalysts [2]; (b) dual catalytic cycles of ethane dehydrogenation and CO_2 activation; (c) transition state structure and isosurfaces of charge density of CO_2 activation on the oxygen vacancy on $CoMoO_x$ surfaces; orange and blue surfaces show electron accumulation and depletion, respectively.

Results and Discussion. Ethane-CO_2, ethane-O_2, and ethane (without oxidant) reactions on Co, Fe, or Ni promoted MoO_x catalysts start with the kinetically relevant C-H bond scission of C_2H_6 on Mo-O site pairs, thus their initial turnovers on fresh catalysts remain identicals (1.4:1.8:1.9 mmol (g-atom Mo s)$^{-1}$, 873 K, 5 kPa C_2H_6, 3.2 kPa oxidant). The rates decrease due to the accumulation of the carbonacious species on the surfaces [1]. Coupled together with the alkane activation is the activation of oxidant, where rates vary with the identity of oxidant as well as that of cation (Co, Fe, Ni) in the Mo-O second coordination sphere [2]. Fig. 1 depicts the proposed dual catalytic cycles of ethane and OC=O activation and their coupling, where C-H bond activation, which reduces the oxide surfaces, is kinetically coupled with the OC=O activation, which replenishes the surface oxygen. Due to this kinetic coupling, the ethane turnovers, which equal the sum of the yields to ethene and reforming products, depend strictly on reverse water-gas shift turnovers (Fig. 1). Incorporating Co into the Mo-O-Co coordination sphere promotes the formation of oxygen vacancies that in turn promote CO_2 activation, leading to higher ethane turnovers and to selective ethene formation, mediated by the increase in reverse water-gas shift turnovers. This reactivity trend confirms that reverse water-gas shift rates are appropriate kinetic descriptors for ethane activation turnovers and also catalyst stabilities during C_2H_6-CO_2 catalysis. Both the vacancy and carboxylate routes are facile for CO_2 activation, but vacancy route prevails at elevated temperatures (973 K) with the transition state shown in Fig. 1. This mechanistic knowledge further allows us to design active sites with dual functionality to enable effective ethene formation.

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Experiments and Kinetic Model Development on Side Chain Alkylation of Toluene with Methanol: An Industrial Perspective

Shamayita Kanungo[1*], Kartick Mondal[1], Vikram Bhide[1]

[1]*Shell Technology Centre, Bangalore, India*
[*] *shamayita.kanungo@shell.com*

Keywords: alkylation, kinetic model, reaction network, industrial processes, technology maturation

Introduction. Ethylbenzene (EB) is an important captive intermediate for Shell, which is currently produced by the reaction of benzene and ethylene. An attractive alternative for EB (and styrene) production is by the side chain alkylation of toluene with methanol due to advantaged/cheaper feedstock. For this technology to replace the existing one, it is important to reach the steep performance targets which in turn requires a better understanding of the underlying reaction mechanism and pathways to the main products (both desired and undesired).

This talk will focus on the reaction network development by a dedicated experiemtal program and kinetic model development. It will give a flavour of technology maturation, in particular how industrial scientists use smart experimentation and simple kinetic models to derive important information that drive decisions on the development of future technologies.

Experimental/methodology. The experiments were conducted in a fixed bed reactor with gas and liquid feeding sections. Typically ~5g of catalyst was loaded, the liquid feed was diluted with N_2 (feed type and dilution depending on the experiment, typical feed partial pressure~1.3 bar_a) and reaction temperature range was 375-405°C. The products were either analyzed online in the gas phase or in certain experiments were condensed downstream and analysed offline.

Results and discussion. The overall outcome of this work is illustrated in Figure 1.

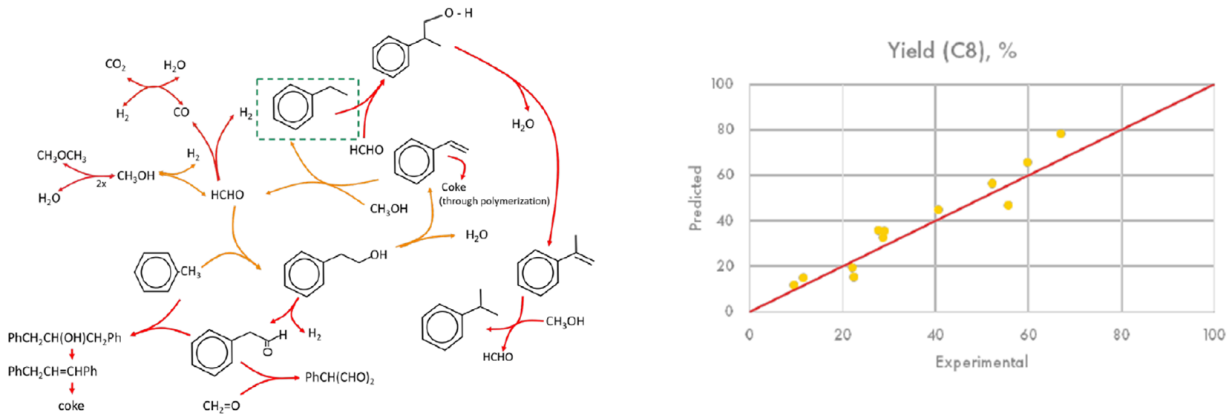


Figure 1 (a) Derived reaction network showing the formation of all major products (d) Modeling results in form of parity plot showing Styrene+EB (C_8) experimental and (model) predicted yield

- A dedicated experimental study was conducted for deriving the reaction network. The pathways to main products as well as to unwanted products which can be potential showstoppers for this technology, were identified.
- Based on the above study and other experiments, *a fit for purpose power law based kinetic model* was developed. This was used to simulate different process concepts which saved crucial experimental time and resources. The outcome from the model helped to make *crucial decisions* in the technology maturation for this process.

Acknowledgments
Jagadeesh Matolli, Sandeep Negi, Jean-Paul Lange, Mary Hyacinth Bastian

References

Internal Shell Reports

MTH over HZSM-5: FASPA, isotope labeling and Kubin-Kucera revisited

C.Liu[1,2], E. Uslamin[1], E. Pidko[1*], F. Kapteijn[2*]

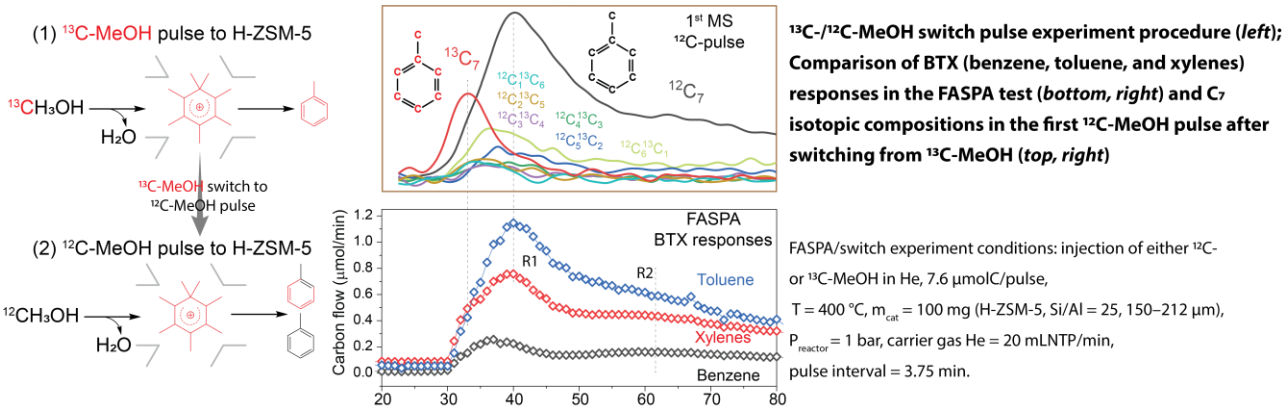
[1]*Inorganic Systems Engineering, Department of Chemical Engineering*
[2]*Catalysis Engineering, Department of Chemical Engineering*
[*]*: Evgeny A. Pidko, e.a.pidko@tudelft.nl*
: Freek Kapteijn, F.Kapteijn@tudelft.nl

Keywords: methanol (MeOH)-to-hydrocarbons (MTH), $^{13}C/^{12}C$ switch, FAst Scanning-Pulse Analysis (FASPA), hydrocarbon pool (HCP) mechanism, isotope labeling

Introduction. Monitoring and revealing complex catalytic pathways under industrially relevant conditions is one of the key challenges in catalysis science. As an example, the kinetic study of MeOH transformations into light hydrocarbons is difficult from a purely experimental point of view due to the complex reaction network, dynamic features of active intermediates, and limited spatial and temporal analysis tools to study the ongoing processes within zeolite micropores under operational conditions.

Experimental/methodology. The switching sequences ^{13}C-labeled and unlabeled MeOH pulses over a model H-ZSM-5 catalyst combined with on-line MS analysis and a newly introduced technique called 'fast scanning-pulse GC analysis' (FASPA) are applied to provide a direct and quantitative insight in the MTH reactions under *quasi* steady-state conditions. The product responses were analyzed using Kubin-Kucera model[1, 2].

Results and discussion.



^{13}C-/^{12}C-MeOH switch pulse experiment procedure (*left*); Comparison of BTX (benzene, toluene, and xylenes) responses in the FASPA test (*bottom, right*) and C_7 isotopic compositions in the first ^{12}C-MeOH pulse after switching from ^{13}C-MeOH (*top, right*)

FASPA/switch experiment conditions: injection of either ^{12}C- or ^{13}C-MeOH in He, 7.6 μmolC/pulse, T = 400 °C, m_{cat} = 100 mg (H-ZSM-5, Si/Al = 25, 150–212 μm), $P_{reactor}$ = 1 bar, carrier gas He = 20 mLNTP/min, pulse interval = 3.75 min.

This FASPA technique allows (sub-)second resolution of the full temporal products response. Upon a MeOH pulse, a very fast primary product formation in the presence of MeOH in a narrow active MTH reaction zone was first observed (R1 in figure), followed by a slower formation of light aromatics (R2), which is closely related to the decomposition and release of HCP species and secondary reactions in absence of MeOH in the downstream part of the catalyst bed.[3] The following isotopic analysis of typical aliphatic C_{3+} product responses after switching ^{13}C-MeOH pulses to the unlabeled MeOH pulses showed a fast isotope scrambling in the formation of C_{3+} species. MS analysis of the light aromatics indicates a complete consecutive but slower isotope incorporation process of ^{12}C into ^{13}C-aromatics. Results provide direct experimental confirmation of the kinetically preferred olefin-based cycle over the aromatics-based cycle. The sequential isotopic incorporation strongly suggests that the paring reaction pathway through aromatic ring contraction and re-expansion steps is operative. In the appearance of aromatics upon pulsing MeOH over larger catalyst beds four processes are directly discerned, involving the displacement of adsorbed species by formed water, isotope incorporation yielding directly labelled and unlabeled products through the paring mechanism and direct aromatization, and HCP conversion through secondary reactions.

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Successful Development of a Taylor-made Catalyst System for Linde´s EDHOXTM Technology

G. Mestl[1*], K. Wanninger[1], S. Böcklein[1], M. Schubert[2], A. Meiswinkel[2], M. Zellhuber[2], F. Winkler[2], N. Schödel[2]

[1]*Clariant AG, R&D Center Heufeld, Waldheimer Str. 13, 83052 Bruckmühl, Germany*
[2]*Chemical Technology R&D, Linde GmbH, Dr.-Carl-von-Linde-Str. 6-14, 82049 Pullach, Germany*
[*]*gerhard.mestl@clariant.com*

Keywords: ODH of ethane, catalyst development, process development, scale-up, M1 oxide

Introduction. Ethylene belongs to the fastest growing chemicals worldwide mainly driven by polyethylene production. Currently, ethylene is manufactured in large-scale, especially in ethane crackers by dehydrogenation in a rather energy demanding endothermic high-temperature process (steam-cracking). Further, acetic acid as another important C2 component is today typically produced by carbonylation of methanol which in turn is produced from natural gas leading to intense CO2 emissions.
Today, the oxidative dehydrogenation of ethane (ODHE) has become a commercially very attractive alternative since the pioneering first investigations by Thorsteinson in the mid 70ties of the last century. In the late 80ties of the last century, Mitsubishi issued a series of ground-breaking patents covering an oxidative dehydrogenation process of ethane utilizing the so-called M1 oxide, which was the starting point for MoVNbTe mixed metal oxides as ODHE catalyst. Since then, many academic and industrial research groups worked on this catalyst material for various alkane oxidation reactions incl. ODHE. But only recently, a collaboration of Linde Engineering and CLARIANT jointly developed an innovative and commercially attractive combination of process, reactor and catalyst design for the ODHE yielding ethylene and acetic acid with very high product selectivities, which is readily available for licensing from Linde (EDHOXTM).

Results and discussion. Two main keys to the superior performance are the multi-layer bed with optimized catalyst properties combined with highly advantageous reaction conditions not only ensuring a stable catalyst operation but also allowing a flexible adaption of the ratio between ethylene and the coproduct acetic acid. Next to the higher overall product selectivity, the ODHE is characterized byzero Scope 1 CO2 emissions. moreover, Scope 2 emissions too can be significantly reduced or even avoided. ODHE is therefore an important enabler to achieve the targeted CO2 reductions in the production of very important key chemicals with high market volumes.

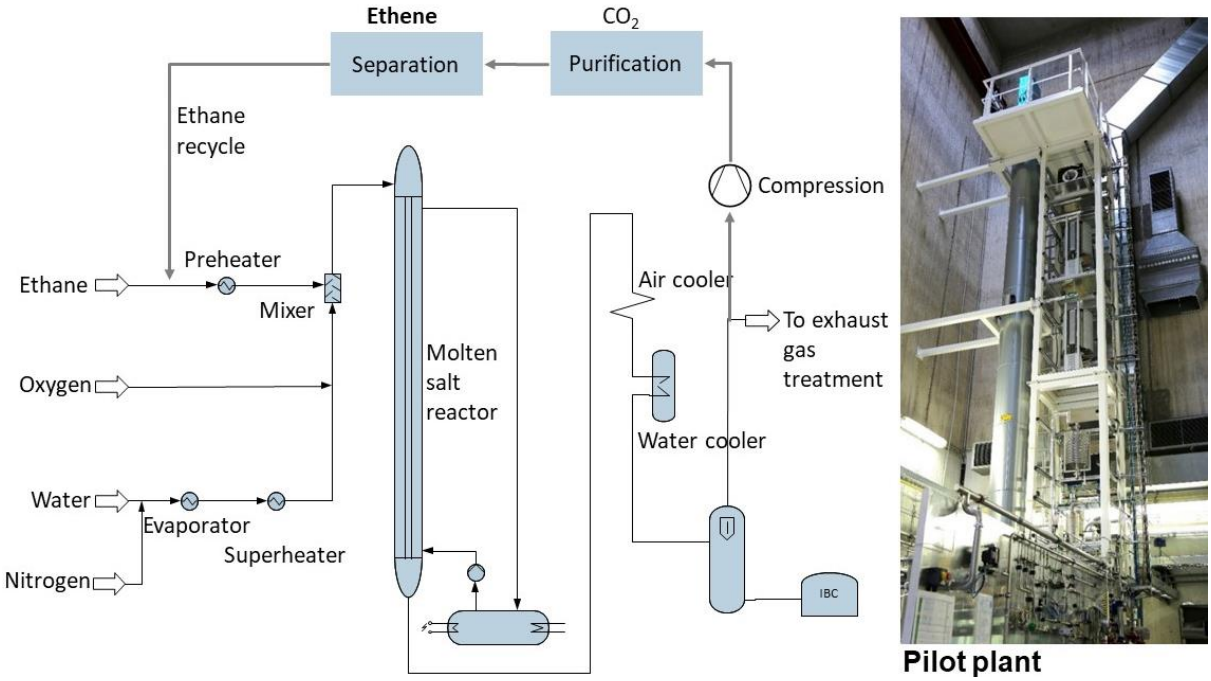

Fig. 1 Scheme of LINDE´s EDHOXTM demo plant

In detail, especially CLARIANT ´sbreakthrough invention of the industrial-scale production of the phase-pure MoVNbTe mixed metal oxide catalyst - exclusively based on cheap, and commercially available raw materials - is an important enabler for the EDHOXTM technology. Eight production unit operations needed to be investigated, scaled-up, and optimized on all equipment scales for guaranteed maximum material yields and minimum raw material losses and waste generation.



Fig. 2 MoVNbTe mixed metal oxide catalyst for the EDHOXTM process

For maximum reactor and process performance, further catalyst properties have been optimized, like the catalyst shape for acceptable pressure drop and optimum filling densities in the saltbath-cooled tube-bundle reactor. In addition, the volume-related catalyst activities were designed such as to achieve the commercially needed one-path ethane conversion levels across the reactor together with the demanded high value-product selectivities to ethylene and acetic acid. It needs to be mentioned here that the ratio between the two value products can be tuned to customer needs by catalyst design and process conditions applied.

Another most important catalyst performance parameter, which had to be tailored, was the required very high oxygen conversion minimizing the remaining oxygen in the reactor effluent still maintaining a minimum concentration required for chemical and mechanical integrity of the catalyst. Further full removal of oxygen can easily be achieved in a separate catalytic downstream step enabling a safe and reliable design of the entire process. All these decisive catalyst parameters for the EDHOXTM process could be successfully developed and proven in a demonstration plant by the joint project team of Linde and CLARIANT researchers.

Plasma catalytic N_2 activation with in-situ product adsorption

Kevin Rouwenhorst, Leon Lefferts*

[1] *Catalytic Processes & Materials, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede (The Netherlands)*
**Corresponding Author l.lefferts@utwente.nl*

Keywords: plasma catalysis, ammonia, NOx

Introduction Although most catalytic conversions studied are thermally activated, alternative excitations methods with photons (photo catalysis) or electrons (electro catalysis) are increasingly importance. A third alternative approach, activation of molecules with electrons in non-thermal plasma, is much less in focus in the catalysis community. However, this approach would enable electrification of the chemical industry, e.g. ammonia and nitric acid production, using processes at mild conditions with operation at flexible scale and with highly flexible load. Besides, non-thermal plasmas excite molecules vibrationally and electronically, without heating all molecules like in thermal activation, which is conceptually very attractive.
This potential has not really materialized at the time, at one hand caused the enormous complexity of physical and chemical effects when combining a non-thermal plasma with a catalytic material [1]. A second reason is that in most cases the energy efficiency is disappointing low because of non-productive relaxation processes in the plasma.
This contribution will show that the presence of catalytic materials in a non-thermal plasma can lead to significant efficiency improvement in plasma catalytic synthesis of NH_3 from N_2 and H_2, as well as plasma-catalytic synthesis of NO_x from N_2 and O_2.

Experimental/methodology All experiments were performed in a quartz tubular reactor with an inner diameter of 4 mm and an outer diameter of 6 mm, at atmospheric pressure. A stainless-steel rod of 1 mm diameter is placed inside the reactor as the high voltage electrode. A metal tube at the outside of the 6mm quartz tube acts as the ground electrode. The temperature was controlled with a thermocouple connected to a heating block around the ground electrode. The product gases were analyzed using an on-line mass spectrometer.

Results and discussion Experiments with H_2/N_2 mixtures in presence of catalysts revealed that the efficiency of ammonia formation was increased with a factor 2 when using zeolite 4A as a catalyst[2], whereas new data show that the efficiency of formation of NO_x from N_2/O_2 mixtures can be improved more than an order of magnitude. The catalyst adsorbs the product (NH_3 or NO_x) and the improved efficiencies are obtained in cyclic experiments: first product is formed and absorbed in presence of plasma, followed by thermal desorption of the produced molecules, i.e. NH_3 or NO_x, in absence of plasma. The improved efficiency is assigned to adsorption of product molecules in the internal surface in the porous catalyst particles, protecting them from decomposition in the plasma.

Our results demonstrate that efficiency of plasma-catalytic conversion can be significantly improved by preventing plasma enhanced decomposition of the product. The main function of the catalyst is in fact protective adsorption. The implications of this with respect to selection of catalysts for plasma catalysis will be further discussed, resulting in the conclusion that in general catalysts active for the same reaction with thermal catalysis, are not preferred.

Acknowledgments *MSc. Samuel Mani and MSc. Sybe Tabak are acknowledged for performing experiments and disussions.*

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Bimetallic Effects in MnMo Catalysts for the Direct and Selective Synthesis of Acetonitrile from NH_3/Syngas Mixtures

M. Elena Martínez-Monje[1], Ali Can Kizilkaya[2], Wilson Henao[1], Patricia Concepción[1], Virginia Pérez Dieste[3], Alexander Missyul[3], Giovanni Agostini[3], Gonzalo Prieto[1,*]

[1] *ITQ Instituto de Tecnología Química, (UPV-CSIC), Valencia, Spain.*

[2] *Izmir Institute of Technology, 35430 Izmir, Turkey.*

[3] *ALBA Synchrotron Light Source, Cerdanyola del Vallès, Barcelona, Spain.*

[*] *Email: prieto@itq.upv.es*

Introduction.

Over the last two decades, significant progress has been witnessed towards the consolidation of carbon and nitrogen renewable cycles, disconnected from resources and energy forms of fossil origin. Coupling these independent chemical cycles via the development of versatile catalytic routes for the formation of C-N bonds from unconventional, e.g. C_1 and N_1 feedstocks, is an attractive strategy towards the sustainable production of nitrogen-containing commodity chemicals. Nitrile synthesis from the direct conversion of ammonia and syngas reaction ($CO+H_2$) mixtures has been reported.[1] However, fundamental knowledge on the true catalyst species and reaction mechanism is required to progress to higher selectivities and catalyst lifetimes. Herein, we present a bimetallic catalyst derived from a crystalline $(NH_4)[Mn_2Mo_2O_8(OH)]$ manganomolybdate precursor which delivers excellent selectivity to acetonitrile (AcCN) alongside remarkable stability. Multi-modal, temperature- and time-resolved characterizations and DFT modelling provide insights into the structure of the catalyst at work and the acetonitrile synthesis mechanism.

Experimental/methodology

A series of ex-ammonium metal (Mn, Co, Ni, Cu, Zn) molybdate catalysts were tested in the conversion of NH_3:H_2:CO mixtures with 2:1:1 (vol) at 3 bar and 723 K. Dynamics in the short- and long-range atomic ordering and near-surface composition of the catalyst during activation and catalysis were studied with T-resolved XANES/EXAFS and HRXRD; and depth-profiling XPS, respectively.

Results and discussion

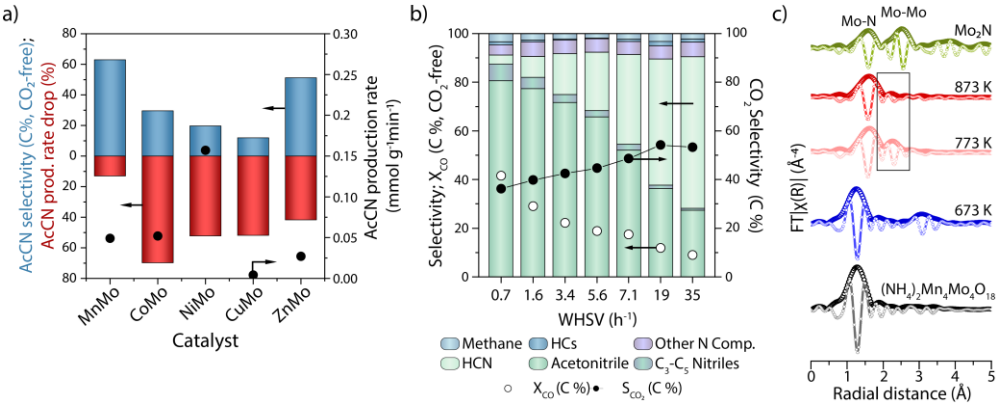

Figure 1 a) AcCN selectivity, production rate and rate drop (after 3h) with MMo catalysts (M=Mn, Co, Ni, Cu, Zn; X_{CO}<18 %); b) Dependence of CO conversion and product selectivity with WHSV for MnMo catalyst; c) T-resolved FT-EXAFS (Mo-K) for the MnMo catalyst precursor exposed to the NH_3/syngas atmosphere (Mo_2N as reference).

Screening of MMo catalysts revealed the superiority of the MnMo bimetallic for a selective and stable production of AcCN (Fig. 1a), achieving a (CO_2-free) selectivity to AcCN >80 % at a CO conversion of 42 % (Fig. 1b). T-resolved XRD showed that the MnMo precursor decomposed into $MnMoO_4$ at 723 K under the reaction atmosphere and swiftly took N up to transform into a cubic metal oxynitride within ca. 1 h at reaction conditions. T-resolved EXAFS revealed that Mn inhibits the growth of MoN_x domains (Fig. 1c) which accounts for the superior catalytic performance with respect to a monometallic Mo_2N benchmark. Our work illustrates how multi-technique studies are essential to identify catalysts which develop only once exposed to process conditions, as well as to rationalize and exploit complex bimetallic effects.

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Zeolite-Catalyzed Cracking of Polyethylene in n-Cetane

M. Matsukata*, Eri Miura, M. Sakai, T. Kamo

[1]*Waseda University, Tokyo, Japan*

Keywords: Plastics, Chemical Recycling, Zeolite, Decomposition, Polyethylene

Introduction.

Currently, ca. 8.2 million tons of waste plastics are discharged annually in Japan, and chemical recycling (CR) is attracting attention as a way to a sustainable society, though the current fraction of chemical recycling has been very low (4%). Due to the mixing of repellent substances in waste plastics, dissolving waste plastics in hydrocarbon solvents and successive separation and removal of repellent substances would improve chemical recycling. The objective of this study was to decompose plastics in hydrocarbon solvent with zeolite catalytically. In this communication, we present our recent results of the decomposition of polyethylene (PE) with Beta zeolite in n-cetane (*n*-C16).

Experimental.

Using a 100 cc batch reactor, 5 g of PE (Mw 35,000), 20 g of *n*-C16, and 50 mg of Beta were placed in the reactor. The reactor was heated to 400°C at a hreating rate of 10°C/min, held for 1 h, and then cooled to room temperature. For comparison, we carried out the experiments without use of Beta and/or PE. The conversion of PE was determined from the weight change of solids. Products were analyzed for their composition using GC-FID, GC-GC, distillation GC, and GPC.

Results and discussion.

Fig. 1 shows the comparison of yields (wt%) obtained with and without PE. Since *n*-C16 was also decomposed with Beta, to clarify the PE-derived products, the denominator was calculated as the sum of the weight of *n*-C16 and Beta. In the presence of PE, the total yield was 120%. The levels of PE and *n*-C16 conversion were 94.1% and 97.9%, respectively. PE was effectively decomposed with Beta at 400°C, while the PE pyrolysis starting temperature is 439°C. It should be noteworthy that Beta directly decomposed PE. The degradation products are mostly aliphatic with aliphatic/aromatics ratio = 5.27 in the presence of PE. More than 90% of *n*-C16 was decomposed in the presence or absence of PE, and the C5-C9 fraction accounted for 56.9% in the absence of PE.

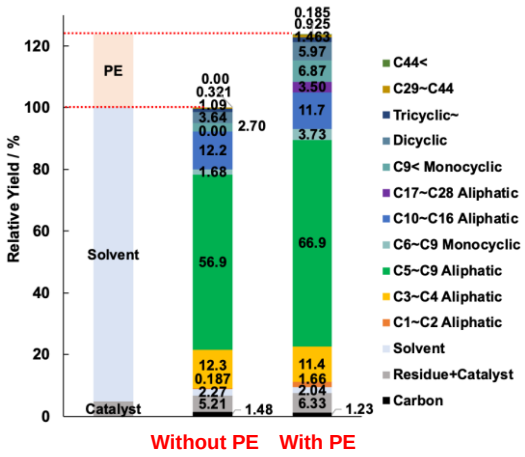

Fig. 1 Comparison of product yields with and without PE.

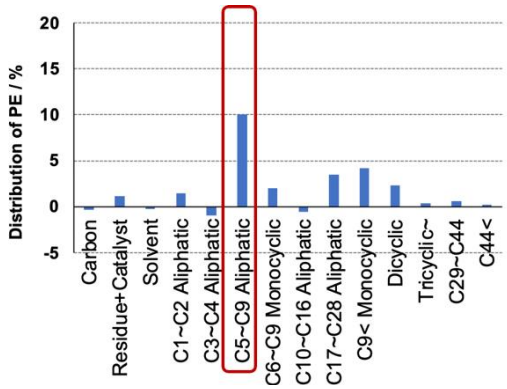

Fig. 2 Relative distribution of decomposition products from PE.

Fig. 2 shows the relative yields of PE-derived products extracted from the difference between the results obtained with and without PE. Among PE-derived products, the C5-C9 fraction was the largest at ca. 10%. The decomposition of PE progressed to lower hydrocarbons equivalent to naphtha fractions, even in the presence of solvents. Other products were mainly straight chain C17-C28 (3.50%), monocyclic aromatics (4.16%), and bicyclic aromatics (2.33%). As for the aromatic products, the primary decomposition product of the linear chains would be aromatized and formed.

Acknowledgments

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Novel green selective oxidation of isoparaffin using O_2 and H_2O on pure oxide catalyst at ambient pressure

M. Ono [1], K. Hiromori[1], N. Shibasaki-Kitakawa[1], H. Yamazaki[2], N. Konishi[2], A. Takahashi[1*]

[1]*Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, Sendai, 980-8579, Japan*
[2]*Mitsubishi Chemical Corporation, Kurashiki, 712-8054, Japan*
**Corresponding author: atsu4.t@tohoku.ac.jp*

Keywords: selective oxidation, isoparaffin, pure oxide catalyst

Introduction. For *t*-Butyl alcohol (TBA) synthesis, one of the industrial processes is the radical oxidation of isobutane under high pressure without a catalyst[1]. This process still has problems of high energy load and low selectivity. As a solution, selective oxidation using Au nanoparticle catalysts at ambient pressure has been reported[2]. In this catalytic reaction, co-existence conditions of H_2 and O_2 are required to generate reactive oxygen species which are effective for selective oxidation, but there are concerns about the risk of explosion. In our laboratory, we have investigated mild selective oxidation using H_2O instead of H_2, and found that mild selective TBA synthesis proceeds under ambient pressure using Au/Co_3O_4 and its rate on only Co_3O_4 support was faster than that on Au/Co_3O_4[3]. The development of this method will lead to economical green conversion of saturated hydrocarbons. In this study, isobutane oxidation experiments were conducted using pure Co_3O_4 under various reaction temperature conditions to investigate the mechanism of selective TBA synthesis.

Experimental/methodology. Commercial Co_3O_4 was used as the catalyst. In oxidation experiments, H_2O (20%) was vaporized and thoroughly mixed with O_2 (10%) + isobutane (10%) + N_2 gas and fed into a packed bed reactor. The reaction temperature was varied at each experiment in the range of 100-200°C as the operating factor. In the analysis, the concentration of products in the effluent was measured by online GC-FID/TCD to determine the formation rate r_i. The selectivity S_{TBA} was calculated based on the total amount of products identified. The adsorbed state of water on the catalyst was evaluated using a temperature programmed desorption with H_2O (H_2O-TPD).

Results and discussion. Figure 1 shows the effect of reaction temperature on the reaction rate for the target TBA and byproducts CO_2. No other products were observed. With increasing temperature up to 140°C, r_{TBA} increased greatly, whereas little CO_2 formation was observed. S_{TBA} reached 83% at 130°C. On the other hand, at higher temperatures above 140°C, only CO_2 production was observed. On the basis of these results, selective oxidation and complete oxidation are considered to be dramatically switched depending on the reaction temperature. Accordingly, Co_3O_4 shows high selective oxidation activity in the specific temperature range, and this is the first report in the world that selective oxidation of hydrocarbons proceeds on pure Co_3O_4 without doping any metals.

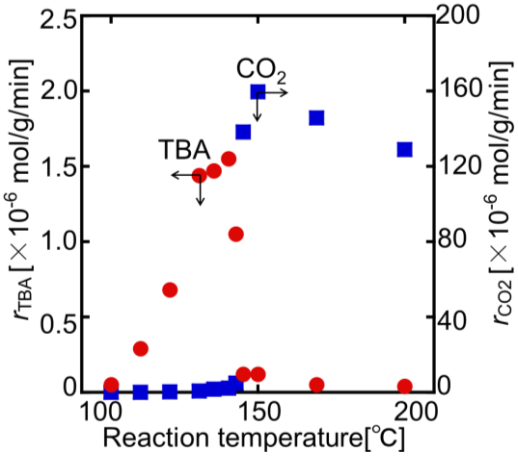

Fig.1 Effect of reaction temperature on r_{TBA} and r_{CO2} using Co_3O_4 catalyst

Now, we focus on the role of water on the catalyst surface. Figure 2 shows the results of H_2O-TPD measurement on Co_3O_4, two peaks were observed. Peak 1 on the low-temperature side is due to physisorption, and peak 2 on the high-temperature side is due to chemisorption. Peak 2 has its top at around 140°C. This indicate that chemisorbed water adsorption/desorption has a significant effect on TBA synthesis. In other words, the role of water on the Co_3O_4 surface is thought to enable TBA selective synthesis.

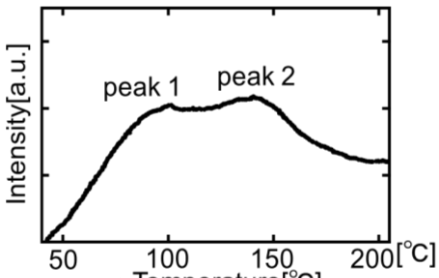

Fig.2 H_2O-TPD profile of Co_3O_4 catalyst

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Investigation of Mo-based dispersed catalysts for the upgrading of heavy oils in slurry reactor

F. Papadopoulou[1,2*], A.A. Lappas[1], E. Heracleous[1,2]

[1]*Chemical Process & Energy Resources Institute CPERI/CERTH, Thessaloniki, Greece*
[2]*School of Science & Technology, International Hellenic University, Thessaloniki, Greece*
[*]*florpapad@certh.gr*

Keywords: Dispersed Catalyst, Mo-octoate, Hydroprocessing, Heavy Oils, Slurry Reactor

Introduction. Due to the increasing global demand for energy, the interest in upgrading heavy oils of bio-, waste-, and fossil-origin by means of hydroprocessing has increased [1]. Heavy oils, depending on the feedstock, are characterized by high content of metals, heteroatoms and impurities, as well as low yields of valuable products. Slurry phase hydrocracking processes, employing transition metal-based dispersed catalysts, can successfully upgrade such difficult feedstocks to lower boiling point fuel fractions and overcome the coking and plugging issues often encountered with fixed-bed reactors [1,2]. In particular, Mo-based catalysts proved to be suitable for cracking and hydrogenation and have been studied under different reaction conditions [2]. In this study, we investigate the hydrotreatment of heavy oil in the presence of Mo-based dispersed and conventional solid catalysts in slurry-type reactor.

Experimental/methodology. The slurry phase hydrocracking of Vacuum Gas Oil (VGO), selected as model feedstock, was conducted in a stirred semi-batch autoclave reactor at 400 °C under constant H_2 pressure (100 bar) for 4 h reaction time. Non-catalytic and catalytic tests were performed with oil-soluble Mo-octoate (15 wt.% Mo) and commercial ex-situ presulfided NiMo-based solid hydrocracking catalyst, at different Mo concentrations (4000 – 12500 wppm Mo). After reaction, the products were separated into gas, liquid, and solid fractions. The gas products were analyzed with GC. The solid was washed with toluene, dried and analyzed (elemental analysis, X-ray diffraction, transmission electron microscopy (TEM)). The liquid product was extensively analyzed (elemental analysis, density, SimDis etc.) to determine the produced fuel properties.

Results and discussion. Figure 1a shows the hydrodesulfurization degree achieved in thermal and catalytic tests with liquid and solid Mo-catalysts at similar Mo concentration. The liquid dispersed catalyst reduces sulfur by ~ 50%, while the conventional solid catalyst achieves higher HDS degree (~ 90%). In terms of hydrocracking, the residue, diesel, and gasoline fractions are similar in all cases (Figure 1b), suggesting that cracking mainly occurs thermally in agreement with literature [2]. In the catalytic tests, high organic oil yields are measured (in the range of ~ 85 wt.%), with no significant difference between tests with solid and liquid Mo-based catalyst. Finally, analysis of the solid product from the tests with liquid Mo-catalyst evidenced the formation of MoS_2 nanoparticles, responsible for the hydrosulfurization activity of the dispersed catalyst.

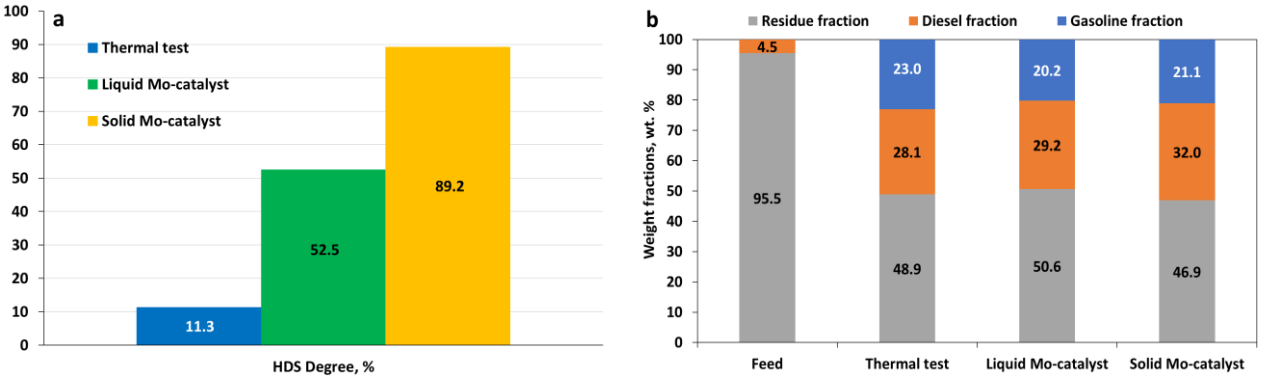

Figure 1. Effect of catalyst on (a) Hydrosulfurization degree (b) Hydrocracking degree

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Overcoming the performance limits of commercial benzyltoluene as liquid organic hydrogen carrier by tuning the isomer composition

T.W. Kim[1], Y. Jo[1], Young-Woong Suh[1*]

[1]*Department of Chemical Engineering, Hanyang University, Seoul 04763, Republic of Korea*
[*]*E-mail: ywsuh@hanyang.ac.kr*

Keywords: liquid organic hydrogen carrier; benzyltoluene; regioisomer; hydrogenation; dehydrogenation

Introduction. The state-of-the-art liquid organic hydrogen carrier (LOHC) molecules, benzyltoluene (H_0-BT) and dibenzyltoluene (H_0-DBT) are available in the market as heat transfer fluids and dielectric media, which are commercially produced in the same process by Friedel–Crafts alkylation of benzyl chloride and toluene over Lewis acids (typically, $FeCl_3$) [1]. This homogeneous catalysis process affords isomeric mixtures of H_0-BT (three regioisomers with *ortho*, *meta*, and *para* linkages [2]) and H_0-DBT (at least eight isomers [3]). Leinweber and Müller reported the different hydrogenation kinetics of *ortho*- and *para*-dominated H_0-BT mixtures [2]. We also found that the isomers of commercial H_0-BT exhibit different hydrogenation rates [4]. This suggests that the isomer structure of H_0-BT can affect its conversion efficiency. Moreover, as each isomer of H_0-(D)BT is not readily available in pure form, one cannot address the effect of the isomer composition on the (de)hydrogenation performance of the isomeric mixtures.

Results and discussion. The study outlines a straightforward strategy to improve the LOHC performance of commercial Marlotherm LH (MLH) [5]. The process started with the synthesis of three H_0-BT regioisomers *via* Friedel–Crafts alkylation of methylbenzyl chloride with benzene, where the dechlorination step is of great importance to obtain a high-purity product. Next, the H_2 storage and release tests demonstrated the superior LOHC performance of the *para* isomer compared to the other isomers. The importance of the *para* isomer was further confirmed using binary and ternary H_0-/H_{12}-BT physical isomer mixtures. Therefore, increasing the fraction of *para* isomer in H_0-BT is the key strategy for improving the LOHC performance. We attempted to meet this requirement by carrying out a one-pot synthesis from benzyl chloride and toluene. Under optimized synthesis conditions, the H-Beta zeolite (SiO_2/Al_2O_3 = 25) afforded the H_0-BT-*p*72 product with a 72% fraction of *para* isomer. This product exhibited superior performance in both hydrogenation and dehydrogenation reactions compared to the MLH-simulated mixture having identical isomer composition to MLH. However, unexpected problems emerged during cycling tests; methylfluorene (MF), formed as dehydrogenation byproduct, significantly reduced the rate of the subsequent hydrogenation. This detrimental issue was overcome by using a Pt–S/Al_2O_3 catalyst, which reduced the fraction of MF to 3%. By adjusting the reaction conditions for H_2 storage over Ru/Al_2O_3 and H_2 release over Pt–S/Al_2O_3, at least 10 interconversions between H_0-BT-*p*72 and H_{12}-BT-*p*72 could be performed continuously at the H_2 storage density level of 6 wt%. Finally, a cost analysis taking into account the material costs along with the LOHC performances demonstrated that H_0-BT-*p*72 is a more suitable option than MLH and *para*-H_0-BT. Therefore, the sequence of investigations discussed above suggests that it may be worth performing further tests on H_0-BT-*p*72 in future process development studies.

Acknowledgments
This work was funded by the National Research Foundation of Korea supported by the Ministry of Science and ICT, Republic of Korea (2019M3E6A1064908).

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Architecture of Industrial Bi-Mo-Co-Fe-K-O Acrolein Catalysts

K. Amakawa[1]*, J. Mauß[1], P. Müller[2], B. Hinrichsen[2], S. Hirth[2],
A. Bader[2], S. Price[3], S. Jacques[3], J. Macht[4]

[1]*Catalysis Research, BASF SE; Ludwigshafen, Germany*
[2]*Analytical and Material Science, BASF SE; Ludwigshafen, Germany.*
[3]*Finden Limited; Abingdon, UK*
[4]*Global Technology Petrochemicals, BASF SE; Ludwigshafen, Germany.*
*kazuhiko.amakawa@basf.com

Introduction

While pure binary bismuth molybdates can perform selective propene oxidation to form acrolein, industrial acrolein catalysts with far higher (factor of > 20) activity are multicomponent molybdate (MCM) system containing at least three promoter elements, namely Fe, Co, and K. Omitting any of them drastically reduces the performance. Here, we reveal the structure of the MCM catalyst and provide mechanistic explanation about how complex structural features are linked to the performance [1].

Experimental/methodology

MCM catalysts with various compositions were prepared via coprecipitation, drying and calcination. Kinetic behavior in propene oxidation was studied in conjunction with structural analysis employing STEM-EDX, XRD, XAS (at Mo, Bi, Fe, and Co edges), XPS, UV-vis, Raman, NH_3-TPD, Propene-TPR, Pyridine-IR, Hg-porosimetry and N_2-physisorption.

Results and discussion

High performance catalyst $Bi_{0.6}Mo_{12}Co_7Fe_3K_{0.1}O_x$, which features a low Bi content compared to binary bismuth molybdates, consists of mixed aggregates of cobalt molybdates, iron molybdate and bismuth molybdate particles (Fig. A). STEM-EDX analysis showed the presence of highly dispersed Bi species besides the bulk α-$Bi_2Mo_3O_{12}$ particles (Fig. B, C). To study the relevance of the highly dispersed surface Bi species, we prepared a catalyst by impregnation of Bi on a Bi-free analog $Mo_{12}Co_7Fe_3K_{0.08}Si_{1.6}O_x$. The Bi-free support material showed low conversion even at temperature of 350°C, whereas the catalyst impregnated with Bi showed the same activity as the reference though it contained 90% less Bi (Fig. D). The result strongly indicates that the highly dispersed surface Bi species formed the relevant BiMoO sites, and in turn, suggests minor role of α-$Bi_2Mo_3O_{12}$ which did not exist in the impregnated sample.
In the presentation, detailed structure-performance relationships regarding the roles of molybdate phases, ion vacancies, and K-promoter will be discussed.

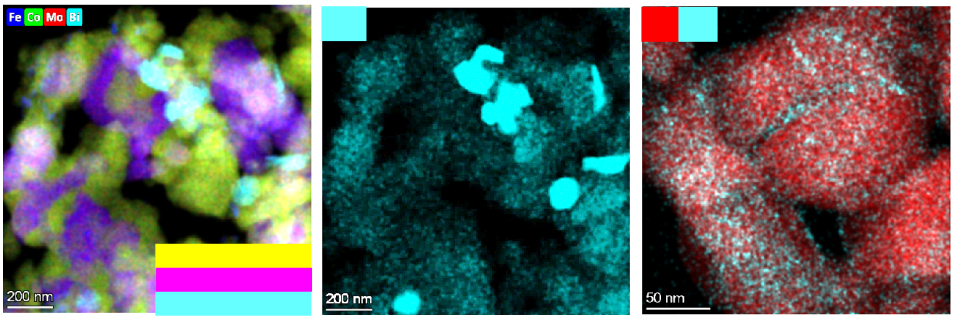

Fig. Analysis and propene oxidation performance of Bi-Mo-Co-Fe-K-O catalysts. (A-C) STEM-EDX images of $Bi_{0.6}Mo_{12}Co_7Fe_3K_{0.1}O_x$. **(D)** Propene oxidation performance of reference catalyst $Bi_{0.6}Mo_{12}Co_7Fe_3K_{0.08}Si_{1.6}O_x$ (ref. Bi0.6), $Mo_{12}Co_7Fe_3K_{0.08}Si_{1.6}O_x$ (w/o Bi), and $Bi_{0.06}Mo_{12}Co_7Fe_3K_{0.08}Si_{1.6}O_x$ (imp. Bi0.06) prepared by post-impregnation of Bi on a Bi-free catalyst. The reaction temperature (T) is shown in the plot area.

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Improved heterogeneous Brønsted acid catalysts for cyclic acetal synthesis

M. Houbrechts[1*], W. Stuyck[1], D. De Vos[1]

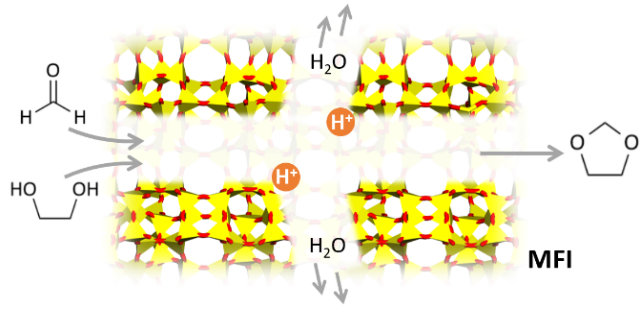
[1]*cMACS, Katholieke Universiteit Leuven, Leuven, Belgium*
[*]*margot.houbrechts@kuleuven.be*

Keywords: Cyclic acetals, Heterogeneous catalysis, Recyclable polymers, Dean-Stark apparatus, Acid zeolite

Introduction.
In recent years, cyclic acetals have been receiving increasing attention as a result of different benefits they can provide. For instance, 1,3-dioxolane (DXL), can be used as a green solvent and as an alternative to more hazardous solvents like THF. In addition, DXL and larger acetals have the potential to be used as monomer for chemically recyclable polymers or as co-monomer in engineering plastics.[1,2] Their performance and use are similar to those of polyolefins, but with the invaluable asset of recyclablility through ring closing depolymerization back to their monomers. Currently, DXL is produced from ethylene glycol using paraformaldehyde or a concentrated solution of aqueous formaldehyde using homogeneous Brønsted acids (e.g., H_2SO_4) or acid resins.[3] We propose that their production can be significantly improved by the use of acid zeolites; the hydrophobic properties can expel the generated water from the active sites while their shape selective properties can steer the reaction selectively to the cyclic acetals instead of undesired oligomer byproducts.[4] In addition, these heterogeneous catalysts ensure easy catalyst recovery. In this work we present the acid catalyzed syntesis of cyclic acetals starting from a diol and aqueous formaldehyde, both abundant and cheap building blocks which can be obtained from renewable resources.

Experimental/methodology.
For the production of 1,3-dioxepane (DXP) from 1,4-butanediol and $HCHO_{aq}$, a Dean-Stark reaction setup was used. For the synthesis of DXL, a water-DXL azeotrope was collected at the top of a distillation.

Results and discussion.
Several commercial zeolites show promising activity towards the conversion of diols and formaldehyde to acetals. For the formation of 1,3-dioxepane (DXP), 12-MR zeolites performed best with a monomer yield of 14% for H-**β** after just 1 hour. This shows a clear increase in monomer yield compared to the commercial Amberlyst-15 acid resin (8% monomer yield). DXL formation is best catalyzed by the 10-MR ZSM-5 zeolite; larger pore zeolites give rise to the formation of larger side products such as 1,3-trioxepane. The optimal Si/Al ratio lies around 25; lower Si/Al ratio renders the zeolite less hydrophobic while at higher ratios the number of Brønsted acid sites decreases. During the recycling test, no significant loss in activity or selectivity was measured.



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We would like to thank the FWO Flanders for funding.

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Room Temperature Plasma-Based Ammonia Synthesis – Designing an Optimal Adsorbent

B.Rolim[2], T.Kristenssen[1,2], C. Hulteberg[1,2*]

[1]Department of Chemical Engineering, Lund University, 221 00 Lund, Sweden
[2]Hulteberg Chemistry & Engineering AB, 212 25 Malmö, Sweden
[*]christian.hulteberg@chemeng.lth.se

Introduction.

Plasma-induced catalysis is an exciting new possibility for producing chemicals at significantly milder conditions than traditional thermal catalysis [1]. As a model reaction, the synthesis of ammonia is typically chosen. Ammonia is an important bulk chemical, representing some 2% of the world energy consumption, mainly fossil fuel-based, and the synthesis is strongly limited by chemical equilibrium [2]. The catalysts traditionally used in ammonia synthesis are iron-based, but also ruthenium has been found to be very active in the reaction. The cost of the precious metal is, however, prohibiting [3]. The plasma synthesis requires slightly different catalyst material, with Ru, Rh, Co and Ni being more active than iron [4]. Based on the reversibility of the plasma reaction, it has been shown that when ammonia is shielded from additional plasma inside a catalyst support structure, the overall ammonia yield increases [1]. However, since the catalyst support adsorption capacity of the ammonia is limited, there is a need for an optimized ammonia adsorbent to shield the product. The ammonia adsorbent should preferably have:

- A high adsorption capacity for ammonia
- A distinct desorption temperature to allow for a controlled release of the ammonia
- A low desorption temperature to avoid too high a temperature that may damage the catalyst

Experimental/methodology.

A number of different adsorbents from the zeolite range are screened for their static adsorption capacity at different temperatures, including room temperature and above the desorption temperature. The static, isothermal adsorption capacity is measured using ammonia in 50 points, ranging from 0.01 mmHg to 500 mmHg. The analysis is performed in a Micromeritics 3-flex unit, and by doing multiple analyses, the chemisorption and physisorption can be separated. The desorption temperature is determined using temperature-programmed ammonia desorption on the same machine. The zeolites are chosen with different pore structures and Si/Al ratios to tune the adsorption capacities.

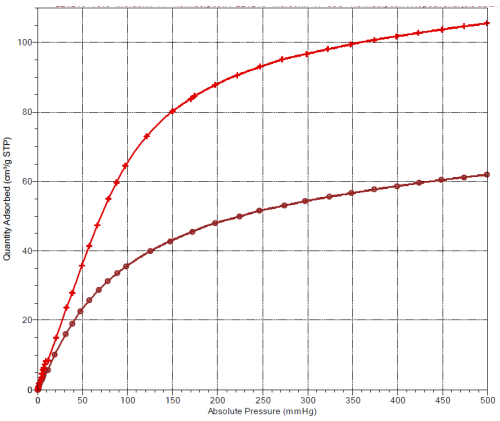

Fig. SEQ Figure * ARABIC 1. Adsorption isotherm

Results and discussion.

Multiple adsorbents have been screened, and the overall adsorption capacity ranges from 0.29-0.76 mmol of ammonia per gram of adsorbent. The more acidic materials typically have wider desorption peaks and thus require higher regeneration temperatures. To avoid broad desorption peaks, an adsorbent with mainly physisorption functionality is preferred.

Acknowledgements

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Hydrothermal Synthesis of Double Metal Cyanide Catalysts for Polyether and Polycarbonate Polyols Production

H.-K. Choi, C. H. Tran, E.-G. Lee, B.-R. Moon, I. Kim*

School of Chemical Engineering, Pusan National University, Busan, Republic of Korea
**ilkim@pusan.ac.kr*

Keywords: double metal cyanide, hydrothermal treatment, polyether, polycarbonate, polyols

Introduction. A series of Zn-Co double metal cyanide (DMC) catalysts have been prepared in the present of various polymeric templates using hydrothermal treatment method. Their activities were evaluated via ring-opening polymerization of epoxides and copolymerization of epoxides and CO_2, which are among the most important processes of DMC catalysis [1-3]. The influence of catalyst preparation parameters such as pH and time of the hydrothermal treatment on the catalytic activity were also investigated.

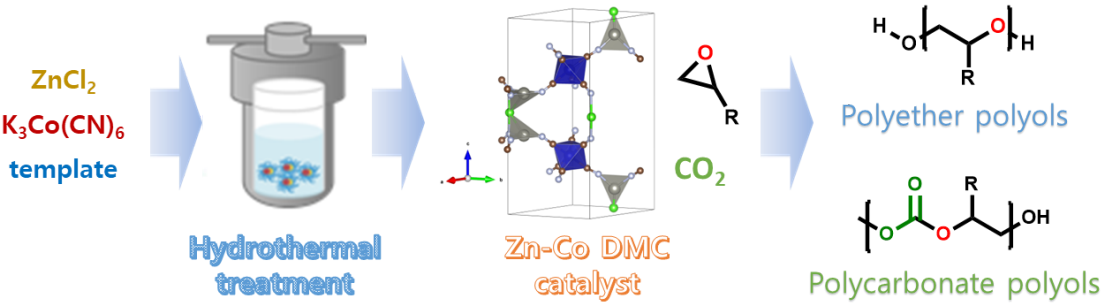

Figure 1. Illustration of the hydrothermal synthesis of DMC catalysts.

Experimental/methodology. Double metal cyanide catalysts were synthesized by hydrothermal treatment using different polymer templates. The chemical structure of the resultant heterogeneous catalysts are characterized by infrared and X-ray photoelectron spectroscopies while their compositions were quantitated by elemental analysis. The catalyst morphology was investigated by X-ray powder diffraction and scanning electronic microscopy. The conversion and carbonate content of the resultant polyols were determined by nuclear magnetic resonance. The thermal properties of the produced polyols were also investigated by differential scanning calorimetry and thermogravimetric analysis.

Results and discussion. The as-prepared DMC catalysts showed relatively high activities for both ring-opening polymerization and copolymerization of propylene oxide and CO_2, producing polyether polyols of very low unsaturation level and narrow dispersity, and polycarbonate polyols with high yield and reasonable carboante content. The polycarbonate properties were also monitored under various conditions such as initial CO_2 pressure, reaction temperature, and amount of initiator.

Table 1. Results for the PO/CO_2 copolymerization acquired by DMC catalysts

Entry	Catalyst	PPC yield (%)	Sco_2[a] (%)	M_n[b] (g/mol)	PDI[c]
1	DMC_L35	72	28	2200	2.31
2	DMC_31R1	67	32	3000	2.91
3	DMC_P123	68	35	3100	2.71

[a]Carbonate content determined by ^{1}H NMR. [b]Number average molecular weight. [c]Polydispersity index.

Acknowledgments

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (2021R1A2C2003685) and was partly supported by a Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korean government (MOTIE) (20208401010080)

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Study of WGS catalyst and CO_2 separation for H_2 production

Cheonwoo Jeong[1*] and Joonwoo Kim[1]

[1]*Particulate Matter Research Center, Research Institute of Industrial Science & Technology, 187-12 Geumho-ro, Gwangyang-si, Jeollanam-do, 57801, KOREA*
[*]*cjeong@rist.re.kr*

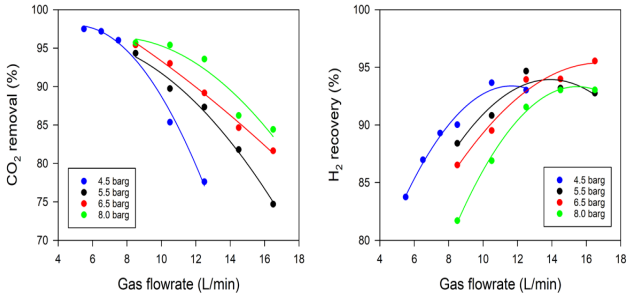
Keywords: medium-temperature shift, hydrogen, carbon dioxide, membrane contactor

Introduction. There are lots of hydrogen production technologies under research such as steam methane reforming, dry reforming and electrolysis etc. Among these technologies, water-gas shift reaction is one of the most feasible one for hydrogen production. The catalyst categorizes into two types depending on working temperature as low-temperature shift and high-temperature shift. Usually each catalyst is packed in two different reactor with heat exchanger resulting in the complexity of process. Thus, the catalyst working in medium temperature was studied in this work. Furthermore, CO_2 is inevitably generated from catalytic reaction. This should be removed from stream, therefore, membrane contactor has studied.

Experimental/methodology. Medium-temperature shift catalyst was prepared in precipitation method. In conventional precipitation(CP), metal ions(Cu^{2+}, Zn^{2+} and Al^{3+}) were precipitated together. After ageing, filter cake was washed and calcined. Before testing performance, catalyst was reduced in reactor. In sequential precipitation(SP), Cu^{2+} and Zn^{2+} were precipitated at first and Al^{3+} was added after 1 h. In order to remove CO_2 in the mixed gas, membrane contactor module was used. In one-side, gas was passed through membrane and deionized water passed through other side. After membrane module, mixture gas was analyzed by gas chromatography and CO_2 removal was calculated.

Results and discussion. SP-CZA was shown better performance compared to CP one. CO conversion of SP-CZA is above 90% from 250 to 450 °C which is known as medium temperature range of WGS reaction. SP catalyst displayed more crystalline structure as zincian malachite than conventional catalyst. Furthermore BET surface area of SP-CZA (44 m^2/g) is larger than CP oxide (33 m^2/g). In CO_2 separation, membrane contactor was tested by using H_2, N_2, CO_2 mixture gas. When injecting more gas in module, contact time between gas and liquid decreases resulting that CO_2 is less removed. Furthermore, in high pressure, CO_2 solubility in water is linearly increased based on Henry's law.

Effect of Gas flowrate and Pressure



- As increasing gas flowrate, less CO_2 and H_2 removed. (More H_2 was recovered)
  → Flowing gas through porous membrane, two gases were not reached to gas and liquid equilibrium.
- As increasing pressure, more CO_2 was removed and less H_2 was recovered.
  → Gas solubility can be increased by Henry's law.
  → Depending on solubility property, gas are solved into water through porous membrane.

Experimental condition
Gas concentration: H_2 43.6%, N_2 12.8%, CO_2 43.6%, Gas flowrate: 5.5–16.5 L/min, Liquid flowrate: 3 L/min,
Pressure: 4.5–8.0 barg, Δ Pressure between gas and liquid: 1.5 bar

Acknowledgments

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Effect of the vanadia structure on the kinetics of methanol oxidative dehydrogenation

G. Galdames[1*], C. Fuenzalida[1], C. Lillo[1], P. Santander[1], R. Jimenez[1], A. Karelovic[1*]

[1]*Carbon and Catalysis Laboratory (CarboCat), Universidad de Concepción, Concepción, Chile*
[*]*ggaldames@udec.cl, akarelovic@udec.cl*

Keywords: Kinetic modeling, methanol, partial oxidation, redox catalysis, acid catalysis.

Introduction. Methanol oxidative dehydrogenation (ODH) products: formaldehyde (FA), methyl formate (MF) and dimethoxymethane (DMM) are interesting as chemical intermediates. This ODH reaction follows a Mars-van Krevelen redox cycle, with the dehydrogenation of a methanol molecule to form adsorbed FA as the rate-determining step (RDS)[1]. It has been suggested that the reaction requires acid sites for the dehydration reactions besides the redox sites for the dehydrogenation reactions [2]. However, there is still lack of clarity on the effect of the physicochemical or structural properties of the catalyst on the reaction kinetics [2,3]. In this work, kinetic models for the formation of the main reaction products are developed for V_2O5/TiO_2 catalysts, to understand the effect of the vanadia surface density on the kinetic parameters.

Experimental/methodology. V_2O_5/TiO_2 catalysts were prepared by wet impregnation varying the vanadia surface density (0.5 to 25 V/nm^2). The catalysts were characterized by XRD and Raman. The reaction was carried out in a packed bed reactor, evaporating CH_3OH into flowing N_2 and air, varying the temperature, residence time and partial pressure of reactants. The effect of water addition to the reactor feed was also studied. The products were detected by gas chromatography. The integral form of the rate equations were solved modeling a 1-D pseudo-homogeneous reactor.

Results and discussion. Based on the mechanism proposed by Iglesia et al. [2], the kinetic models shown on figure 1.a were developed and fitted for the net formation of FA, MF and DMM, on 2.5 and 15 V/nm^2. A parity plot and an example of experimental vs simulated data are shown in figure 1.b and 1.c, respectively.

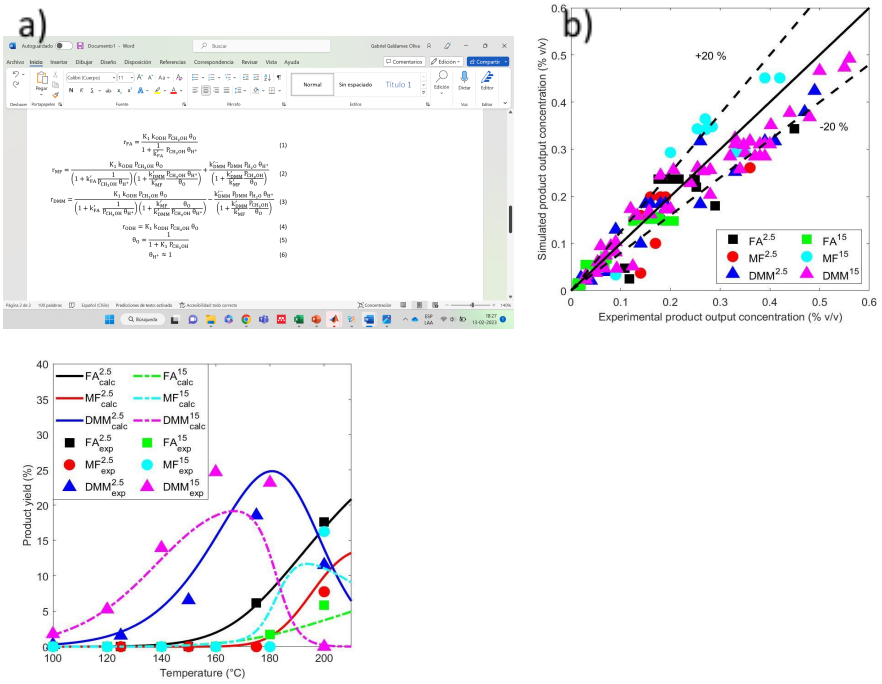

Figura 1. a) Kinetic models for the formation of ODH products, b) Parity plot for measured and predicted FA (squares), MF (circles) and DMM (triangles) concentration in the product stream and c) Simulated vs experimental FA (squares), MF (circles) and DMM (triangles) yields (GHSV = 20 L/(h gcat), $CH_3OH/O_2/N_2$ = 4/4/92% v/v)

The K_1k_{ODH} apparent activation energy is similar for both catalysts (-8 and -7 kJ/mol). The difference of activity its attributed to the higher enthalpy of CH_3OH adsorption at 15 V/nm^2 (-103 kJ/mol) compared to 2.5 V/nm^2 (-82 kJ/mol): 15 V/nm^2 has a stronger interaction with the redox sites, attributed to the different

type of lattice oxygen atoms in the multilayer crystalline VOx domains observed at surface densities larger than 8 V/nm^2, by XRD and Raman. The model adequately simulates the reaction, with mean errors around the 20% (Figure 1.b) and accurately predicts the trends of product yield at the studied reaction conditions, with DMM as the main product at lower temperatures and higher FA and MF yield as the temperature rises (Figure 1.c). At higher temperatures, the total oxidation of CH_3OH leads to CO and CO_2 as the main products.

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Green hydroxylation and ketonization of polyethylene using titanosilicate catalysts

R. Lemmens[1*], J. Vercammen[1], D. De Vos[1]

[1] *cMACS, KU Leuven, Belgium*
[*] *robin.lemmens1@kuleuven.be*

Although polyethylene (PE) is the most common plastic in the world, its applications are limited by the lack of functional groups. The introduction of hydroxyl and carbonyl groups through a post-polymerization C-H bond oxidation step can impart desirable properties, such as paintability and adhesion. Provided that the level of functionalization is sufficiently low, the favorable properties of the virgin PE (*e.g.,* mechanical strength) are perfectly retained, thus rendering the functionalized polymer potentially more valuable [1,2].

Recently, the research group of John F. Hartwig reported an efficient catalytic system for the oxidation of PE, nicely showing the improved applicability of the functionalized polymer, while retaining the beneficial properties of the virgin PE. However, a homogeneous ruthenium catalyst with a perfluorinated porphyrin ligand are employed, along with an atom-inefficient oxidant, in a chlorinated solvent [1].

In this work, PE oxidation was attempted with environmentally benign peroxides, using titanosilicate catalysts in a non-chlorinated solvent. Although titanosilicates are mostly known for epoxidation, also the oxidation of alkanes, yielding alcohols and ketones, has been known for decades [3,4]. For this conversion, an oxygen rebound mechanism (see figure) was hypothesized, involving a rapid recombination between the formed alkyl radical, and the peroxide molecule activated by a Ti-center, yielding an alcohol (a). In the following step (b), the alcohol can similarly be converted into a ketone. Owing to the rapid transfer step, no radicals are set free, thereby providing a highly selective route towards secondary alcohols and ketones [3].

Since the interaction of a polymer with Ti-centers inside a microporous framework represents a challenging task, this research focused on titanosilicates with large external surface areas, to render a large fraction of the Ti-centers accessible for the polymer [5,6]. First, various titanosilicates were screened in the oxidation of alkanes, to optimize the reaction conditions in terms of yield and selectivity. The optimal conditions were then applied in the oxidation of LDPE, MDPE and HDPE. For each type of PE, at least 2 % functionalization (1 C=O group per 50 C atoms) could obtained, with peroxide efficiencies up to 25 %. It was shown that the crystallinity of the virgin PE is retained in the functionalized PE, while thermal stability is slightly increased.

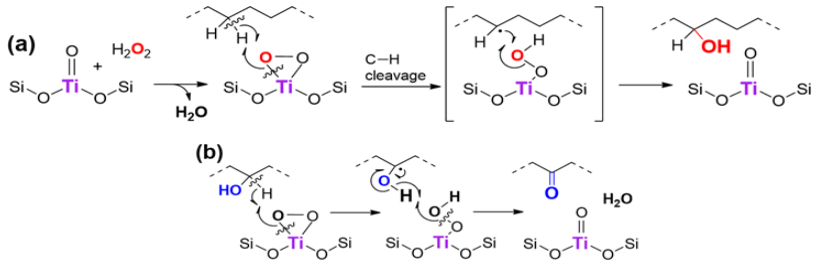

Figure: Oxygen rebound mechanism for the oxidation of C-H bonds employing H_2O_2 and a titanosilicate catalyst.

Acknowledgments
We are grateful to the FWO-Vlaanderen for the funding of this research project (scholarship 1S85822N).

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Catalytic valorization of plastic waste pyrolysis non-condensable gases towards propylene production

Ehsan Mahmoudi[1], Stavros A. Theofanidis[1,2], Angeliki A. Lemonidou[1,3*]

[1]*Department of Chemical Engineering, Aristotle University of Thessaloniki, University Campus, 54124 Thessaloniki, Greece;* [2]*AristEng S.à r.l., 77, Rue de Merl, L-2146, Luxembourg City, Luxembourg;*

[3]*CPERI/CERTH, P.O. Box 60361 Thermi, Thessaloniki 57001, Greece*

**Corresponding Author: alemonidou@cheng.auth.gr*

Keywords: Plastic Recycling, Propylene Production, Cross-Metathesis Reaction, Tungsten Oxide, Catalysis.

Introduction.

Plastic waste, instead of traditional landfill and incineration can be converted to valuable chemicals and fuels. Pyrolysis is a promising method for converting plastic waste to value-added products and has advantages, such as simple operation and low-cost technology, enabling the processing of a wide range of feedstocks. Pyrolysis is a thermal decomposition method at high temperatures (300-1000°C) in an inert atmosphere. The three main products of pyrolysis are: solids (char), liquids (pyrolysis oil) and gases (non-condensable gases, NCGs). NCGs mainly contain light olefins such as ethylene, propylene, and butenes. Propylene is a major commodity chemical playing a leading role in the market. However, the disparity between supply and demand created the so-called propylene gap, which highlights the necessity for on-purpose propylene production[1, 2]. The propylene gap in Europe has been estimated at 347 kt in 2021. Consequently, this work aims at valorizing the NCGs, produced via plastic waste pyrolysis, through the cross-metathesis reaction of butenes and ethylene to propylene.

Experimental/methodology.

A thermodynamic analysis was performed using Aspen Plus® V9 software. Catalyst synthesis: x-WO_3 catalysts were synthesized via the wet impregnation method (x=10, 15, 20, and 25 wt%) on Al-MCM-41. The samples were calcined at 600°C under airflow for 4 hours, labeled as "x-WO_3-Al-MCM-41". Catalytic tests: A parametric study was performed in a fixed bed reactor at P_{tot}=1 bar, investigating the effect of temperature (450-600°C), W_{Cat}/F^0(1.3-5.3 $kg_{Cat}\cdot s\cdot mol^{-1}$), ethylene/1-butene molar ratio (0-4.5).

Results and discussion.

To maximize the propylene yield, the optimum cross-metathesis reaction conditions were determined, based on thermodynamic calculations. Pressure and ethylene/1-butene feed ratio showed minimal to no effect on propylene yield, whereas a peak maximum was shown in the case of temperature at 540°C. The support Al-MCM-41 is active, converting 1-butene up to 90%; nevertheless, the selectivity towards propylene was very low, with major products being 2-butene and isobutylene, suggesting isomerization activity. The addition of WO_3 further improved the catalytic activity and selectivity towards propylene. The best candidate, 20%WO_3-Al-MCM-41 reached propylene selectivity of 32% at a conversion of 88% and 8% for 1-butene and ethylene, respectively, during the metathesis reaction at 550°C, P_{tot} =1bar, W_{Cat}/F^0=2.6 $kg_{Cat}.s.mol^{-1}$ and ethylene/1-butene ratio = 4.5. Furthermore, results over the latter catalyst highlighted that after 4 hours of reaction, there was no evidence of catalyst decay. Oxygen temperature programmed oxidation of the used catalyst revealed coke deposition equal to 0.37 wt% ($C_{deposited}$/ g_{Cat} %).

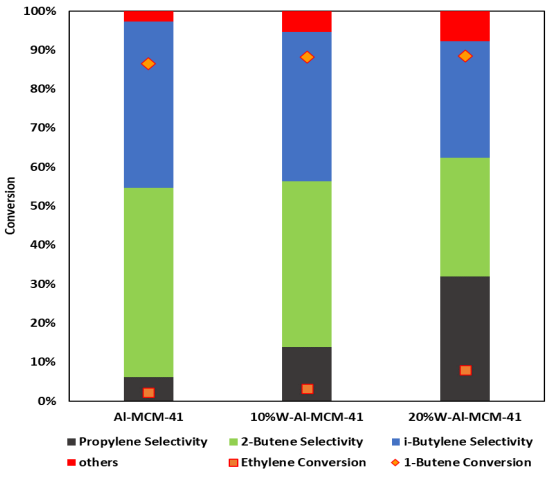

Fig1: 1-Butene, Ethylene conversion and product selectivity, during metathesis at 550°C, W_{Cat}/F^0=2.6kg_{Cat}.s.mol^{-1}, C2$^=$/1-C4$^=$=4.5.

Acknowledgments

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Synthesis of terephthalic plasticizer from waste poly(ethylene terephthalate) in the presence of organotin catalyst

***Marcin Muszyński*[1,2]**, *Agata Krasuska[1], Janusz Nowicki[1], Gabriela Maria Dudek[2], Ewa Nowakowska-Bogdan[1], Maria Bartoszewicz[1]*

[1] Łukasiewicz - Institute of Heavy Organic Synthesis, Kędzierzyn-Koźle, Poland

[2] Silesian University of Technology, Gliwice, Poland

marcin.muszynski@icso.lukasiewicz.gov.pl

Keywords: Recycling, alcoholysis, chemical recycling, catalysis

Introduction.

Poly(ethylene terephthalate) is one of the most widely used polymers worldwide. Its annual production have reached over 50 MT in 2016 and it is estimated that 32 MT of PET waste was generated in 2015 worldwide [1,2]. Despite of increased regulatory pressure aimed at increasing recycling of waste plastics most of produced PET waste remains unrecycled or it is used for energy generation. Chemical recycling of PET is usually carried out via hydrolysis or glycolysis of waste polymer to obtain terephthalic acid or PET oligomers which can be used in further synthesis of PET. PET alcoholysis with 2-EH is a process that is not widely described in scientific literature although reaction using organotin catalyst has been known using organotin catalyst [3], zinc and titanium compounds in the presence of ionic liquids [4].

Experimental/methodology. The text should be 11-point Calibri.

Catalyst screening tests were conducted in glass reactor equipped with a temperature control system, a mechanical stirrer, an azeotropic cap and a reflux condenser. The azeotropic cap was filled with about 75% distilled water, and the rest was supplemented with 2ethylhexanol (2-EH). The presence of water allows for the effective removal of ethylene glycol (EG) formed as a result of the reaction and separation and the return of 2-ethylhexanol. Post-reaction mixture was purified by washing to remove catalyst and ~~by~~ obtained crude product was distilled in reduced pressure to remove excess of alcohol. Product obtained this way was used as a PVC plasticizer. Another sample was additionally purified by further distillation in reduced pressure to obtain clear TFDO free of pigments that were present in undistilled product. Plasticization properties of obtained samples were tested using standard PVC mixtures.

Results and discussion.

Tests were performed using two application samples obtained from depolymerization of waste PET and results were compared commercially available *bis*(2-ethylhexyl terephthalate). All of tested samples had similar hardness and only sample obtained using colour TFDO showed only slightly higher density. Tensile strength and elongation were at similar levels with compared to sample containing pigments and higher boiling byproducts and exhibiting slightly higher plasticizing properties regarding elongation at break. This might be caused by the presence of PET oligomers in undistilled plasticizer. Sample obtained with the use of unpurified plasticizer also exhibits noticeably lower plasticizer migration which can also be attributed to the presence of PET oligomers which did not undergo full depolymerization and therefore are less prone to migration from the PVC mixture. The obtained results show that plasticizers synthesized with the use of waste PET are characterized by good plasticizing properties.

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Brønsted acid catalysis opens a new green route to thiolactide, a monomer for novel and potentially sustainable polythiolester materials

An Sofie Narmon[1,2], Ibrahim Khalil[1], Gleb Ivanushkin[1], Michiel Dusselier[1]*
[1]*Department of Microbial and Molecular Systems, Center for Sustainable Catalysis and Engineering (CSCE), KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.*
[2]*B4Plastics BV, IQ-Parklaan 2A, 3650 Dilsen-Stokkem, Belgium.*
michiel.dusselier@kuleuven.be

Introduction.

Poly(lactic acid) (PLA) is one of the most prominent biobased and biodegradable polyesters (PEs). PLA is currently made by ring-opening polymerization of lactide (LD), which is industrially made by backbiting depolymerization of polycondensed lactic acid (LA), a time- and energy intensive process. Novel routes to LD have been reported recently.[1] For one, our lab developed a shape-selective zeolite-based catalytic process, enabling the one-step conversion of LA to LD in high yield and preserving the stereochemistry of LA.[2,3] While PLA is widely studied, research on its sulfur containing analog, poly(thiolactic acid) (PTLA), is only just starting. Polythiolesters (PTEs), such as PTLA, are known to often show enhanced thermal, mechanical, electrochemical, and optical properties compared to PEs. Moreover, they regularly show enhanced depolymerizability (e.g. chemical recycling, alkaline hydrolysis, photolysis)[4]. Despite these promising features, no industrial syntheses currently exist. One possible reason is the limited amount of efficient and sustainable synthesis methods for thiodilactones. Synthesis routes toward thiolactide (TLD), the sulfur analog of LD, directly from TLA have only been published very recently (2021).[5,6] However, these methods use coupling agents in stoichiometric or excessive amounts, reducing atom efficiency and resulting in waste products. In addition, the reactions are stoichiometric or homogeneously catalyzed and some very toxic compounds are used and formed. Here, we describe a novel one-step synthesis route to TLD from TLA in high yields and in the absence of toxic sacrificial reagents by Brønsted acid catalysis.

Experimental/methodology.

In a typical reaction 0.5 g of TLA is added to a 10 mL round bottom flask, together with 0.2825 mmol H^+ (i.e. zeolite, ion exchange resin or p-toluenesulfonic acid (p-TSA)). 5 mL of solvent is added (toluene or o-xylene) and the mixture is heated till reflux for 24-72h. A Dean-Stark trap, filled with the same solvent, is used to remove water. The crude reaction mixture is analyzed by ^{1}H-NMR (400 MHz, dmso-d6), HPLC, and chiral GC.[7]

Results and discussion.

A novel synthesis route to TLD by the direct condensation of TLA with Brønsted acid catalysts in the absence of sacrificial reagents is presented. Homogeneous sulfonic acids, such as p-TSA, proved to be very effective and an excellent TLD yield of 80% and a volumetric productivity of 11.2 g_{TLD} L^{-1} h^{-1} were obtained (mesitylene, 24 h).[7] In addition, this method improved the atom economy ((molar mass of desired product/molar masses of reactants)*100) of the other reactions in literature with 63-88% and reduced the ecology factor (mass of total waste/mass of product) by 66-97%. However, heterogenizing the catalytic system for this reaction was challenging. Sulfonic acid containing ion-exchange resins afforded a maximum TLD yield of 39%. Even though proven to be very successful in the synthesis of LD from LA, an even lower yield was obtained with Brønsted acid beta zeolites (up to 28%). Reasons for these differences were investigated. First, TLA showed a lower tendency toward (poly)condensation than LA, reducing the need for shape-selective catalysis. Second, very strong interactions of TLA, compared to LA, with the zeolite were seen by FT-IR (Fourier-Transform Infrared) and hypothesized to counteract catalytic activity and induce diffusion limitations or sulfur poisoning. As a proof of concept, TLD was purified and polymerized with triethylamine as the catalyst to chains with a weight-average molar mass up to 56 kg mol^{-1}.

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Effect of support on Ru-based catalysts in oxidation of nitric oxide for nitric acid production

J. Gopakumar[1], B.C. Enger[2], D. Waller[3], M. Rønning[1*]

[1]*Norwegian University of Science & Technology (NTNU), Trondheim, Norway*
[2]*SINTEF Industry, Kinetic & Catalysis group, Trondheim, Norway*
[3]*YARA Technology Center, Porsgrunn, Norway*
[*]*magnus.ronning@ntnu.no (M. Rønning)*

Keywords: Nitric Oxide, Nitric Acid, Industry, Ruthenium, Ceria, Alumina, Zirconia, Titania

Introduction: Nitric acid is an important chemical building block & is produced industrially by the Ostwald process, where ammonia is oxidized by atmospheric oxygen using Pt-Rh gauze catalysts to yield nitric oxide [1]. The typical NO concentration at the exit of the ammonia combustor is 10% [1], & NO is further oxidized in a homogeneous gas phase reaction to NO_2. NO_2 is absorbed in water to yield nitric acid. Use of a low temperature catalyst to oxidize NO to NO_2 is a sustainable alternative to reduce the industrial CAPEX. This is achieved by replacing the homogeneous oxidation process by a compact heterogeneously catalysed process. There is hardly any literature on catalytic NO oxidation at high concentrations, but a large body of literature on diesel engine exhaust treatment with NO concentrations at ppm level. In our in-house research, supported Ru shows promising performance compared to other catalysts at industrial conditions [2].

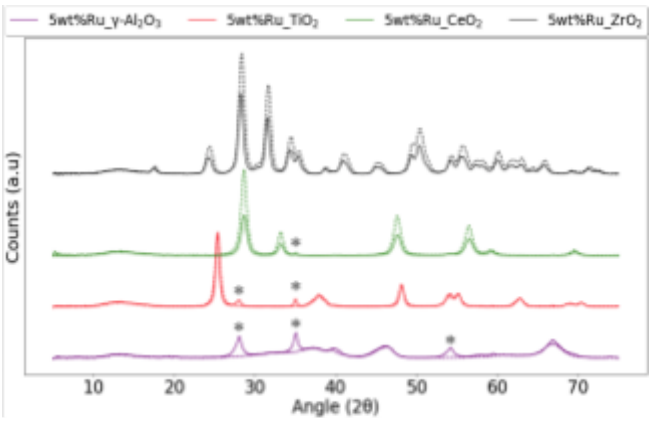

*Figure 1: XRD patterns recorded for different supported 5wt%. Ru catalyst samples in the 2θ range 5-75˚: **Catalysts** – & **Supports** - -; Peaks of RuO_2 is marked as **.***

Experimental/methodology: All catalysts were prepared using *incipient wetness* impregnation with 5wt%. Ru, & pre-calcined in synthetic air for 2hrs at 450°C. The following supports are studied in this work: ZrO_2, CeO_2, TiO_2, & γ-Al_2O_3. NO oxidation activity is evaluated by subjecting the catalysts to two different feeds (i) & (ii) (refer Figure 2), as a function of temperature (250 – 400°C) at atmospheric pressure. *In-situ* XAS-XRD will be performed February 2023, & the results will be used to discuss Ru behaviour during NO oxidation with respect to the two different feeds.

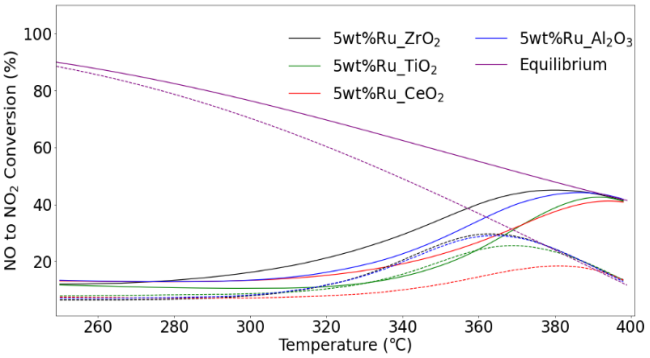

*Figure 2: Conversion of NO to NO_2 using 5wt%Ru on different supports in the presence of feed (i) & (ii) at 1bar: **Feed (i)** – 10%NO, 6%O_2, 15%H_2O & balance Inert & **Feed (ii)** - - 5%NO, 5% NO_2, 3.5%O_2, 15%H_2O & balance Inert*

Results & discussion: Figure 1 present X-ray diffractograms & Figure 2 present NO conversion results of Ru-based catalyst on different supports. Supported catalyst perform better than the other three supported catalyst in feed (i). The activity of Ru on all supports is significantly reduced when the feed was changed to feed (ii) (Figure 1), which indicates NO_2 inhibition. 5wt%Ru/ZrO_2 & 5wt%Ru/Al_2O_3 had similar activity in feed (ii).

Acknowledgements: This project is funded by iCSI center from the Research Council of Norway.

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Lowering the operating temperature of Au acetylene hydrochlorination catalysts using oxidised carbon supports

S. Pattisson[1*], S. Dawson[1], G. Malta[1], N. Dummer[1], L. Smith[1], A. Lazaridou[1], D. Morgan[1], S. Freakley[2], S. Kondrat[3], J. Smit[4], P. Johnston[4], G. Hutchings[1]

[1] *Max Planck Centre on the Fundamentals of Heterogeneous Catalysis, Cardiff Catalysis Institute, UK*

[2] *Department of Chemistry, University of Bath, UK*

[3] *Department of Chemistry, Loughborough University, UK*

[4] *Johnson Matthey, UK*

[*] *Pattissonsd@cardiff.ac.uk*

Introduction. The replacement of the toxic mercuric chloride acetylene hydrochlorination catalyst represents a major landmark in catalysis. Despite the successful commercialization of a gold catalyst, the challenge remains to identify catalysts that can operate at lower temperatures. Light-off temperature is a critical factor in applying gold catalysts to existing reactors, and catalysts must be able to operate within the available temperature range dictated by reactor design. Various methods have been used to increase the activity of gold catalysts such as the use of promoters, modification of the support, and incorporation of additional metals, however few studies focus specifically on light-off temperature. Surface oxygen functionality has been shown to influence the activity of gold[1] and other metals[2] for this reaction, with higher activity often being accompanied by poor stability. These studies often focus on relatively low O at.%, either studying commercial supports or mild oxidation methods. This work studies the effect of harsher oxidation methods on overall activity and light-off temperature of gold catalysts for vinyl chloride monomer (VCM) production [3].

Experimental/methodology. A series of oxidised carbon supports were prepared using a modified Hummers oxidation technique whereby the extent of support oxidation was controlled by using varied amounts of potassium permanganate (0-10g/5g carbon support). Gold was then deposited on the oxidised supports using the standard aqua regia method. Catalysts were characterised using XRD, XPS and XAS. All catalysts were tested for acetylene hydrochlorination under dilute conditions over a range of temperatures (140-200 °C) using a GC fitted with an FID detector for online analysis.

Results and discussion. XPS demonstrates that a range of O at.% was achieved by varying the amount of oxidant. After Au was supported on oxidized carbon, all catalysts demonstrated an increased activity at 200 °C when compared to the standard Au/C (Figure 1a). An optimum level of oxidation of ca. 18 O at.% is apparent, after which further oxidation leads to lower activity catalysts due to collapse of the pore structure and dramatic loss of surface area, confirmed using N_2 physisorption. The stability of these modified materials is low, with rapid deactivation being observed due to sintering of the gold and loss of the atomically dispersed active species. In addition, each of these materials displayed a remarkable low-temperature activity when compared to the Au/C standard with an apparent correlation between increasing O at.% and lower light-off temperatures (Figure 1b). C-O functionality, in the form of phenol, carboxylate and ether, was found to be a key descriptor of low temperature activity with relative concentration of C-O directly correlating with light-off temperatures, even when considering literature catalysts prepared by alternative oxidative treatments[1,4].

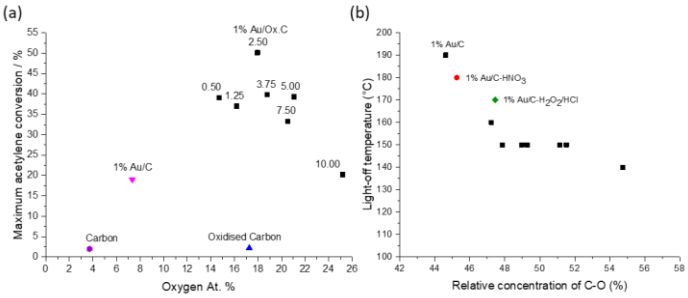

Figure 1. a) O at.% of the ox. carbon supported Au catalysts (■), Au/C standard (▼), oxidized (▲) and unoxidized (⬢) metal-free carbon versus maximum acetylene conversion. b) Light-off temperatures for Au/C (▼), ox. carbon supported Au catalysts (■), Au/C-H_2O_2/HCl (◆) and Au/C-HNO_3 (●) against relative conc. of C-O (%).

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Extrusion of Optimized Catalysts with Smart Extrusion Technology from ECT-KEMA – Perspectives and Potential –

Torsten Seidel[1*], Martin Simon[2]

[1]*ECT-KEMA GmbH, Görlitz, Germany*
[2]*ECT-KEMA GmbH, Görlitz, Germany*
[*]*info@ect-kema.de*

In recent years, ECT-KEMA GmbH has widened its range of auger and piston extruders for the extrusion of catalysts with different geometries in a goal-oriented process and developed a set of tools that can be used to optimize the extrusion of catalysts.
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3. Permanent optimization of wear technology based on the latest findings in coating systems for monolithic augers made of ceramic or carbide.
4. Supply of dies and pressure heads made of different materials – if wanted as well support to optimize the die geometry based on material specific simulations of the extruded masses of the customer.
5. Selective temperature control of all components that come into contact with the ceramic body like auger, barrel, pressure head and die – essential for temperature-sensitive bodies.
6. With sensor systems applied for ECT-KEMA in combination with newly developed cutting technology, we have succeeded in extruding catalysts with near-constant L/D ratio and if wanted to round off the extruded pellets into granulates.

Development of integrated solutions from preparation, optimization of the formulation in our laboratory, cutting and handling of the green extrudates.
We are looking forward to the talks and contacts at Europacat 2023 in Prague.

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Identification of significant parameter in the Ostwald process using statistically optimized experimental designs

L.-C. Stoltenberg[1*], F. Kornemann[1], F. Biermann[1], A. Wiser[2], C. Renk[3], A. Orth[4], A. Drochner[1], M. Votsmeier[1,2], B.J.M. Etzold[1]

[1]*Technische Universität Darmstadt, Ernst-Berl-Institut, Alarich-Weiss-Straße 8, D-64287 Darmstadt*
[2]*Umicore AG & Co. KG, Rodenbacher Chaussee 4, D-63457 Hanau-Wolfgang*
[3]*Thyssenkrupp Industrial Solutions AG, Friedrich-Uhde-Straße 15, D-44141 Dortmund*
[4]*Umesoft GmbH, Steinbacher Str. 14, D-65760 Eschborn*
[*]*lars-christian.stoltenberg@tu-darmstadt.de*

Keywords: Ostwald Process, Design-of-Experiment, Laughing gas

Introduction. The industrial production of nitric acid - and consecutively fertilizers - through the Ostwald Process represents one of the key technologies in our modern society, with an annual capacity of more than 100 million metric tons HNO_3 globally.[1] While the oxidation of ammonia over Pt-Gauzes exhibits practically full conversion and remarkable high selectivities of 95 - 97 % to nitric oxide, it still leaves room for improvement.[2,3] The remaining selectivities are roughly equally distributed between elemental nitrogen and dinitrogen oxide (laughing gas).[2] Both represent an economic loss, but the latter also acts as a potent greenhouse gas as well as an ozone-depleting substance.[3] Considering the global scale of the process, even miniscule emission reductions can have a profound impact. While several approaches for laughing gas reduction already exists on an industrial level, most of them focus on mitigating the emissions via postprocessing instead of lowering the formation in the first place.[4]

Experimental/methodology. The technological requirements necessary to study the Ostwald process on laboratory scale are quite considerable. Mimicking the industrial conditions alone, however, does not suffice for a sound design of experiment due to the narrow parameter range. Hence, the setup even has to exceed the harsh conditions by allowing for short residence times (~1 ms), higher reaction temperatures (up to 1100 °C), ammonia volume fractions just below the explosive limit (13 vol-%) and preheating temperatures (up to 450 °C), combined with pressure up to 5 bar. While this is challenging on its own, an increased level of control and reproducibility is required to minimize statistical noise in the generation of data. The presented setup allows for the independent setting of the preheating and the heating mantle temperature, the pressure, the volume flow, and the ammonia volume fraction. The design themselves are specifically chosen to extract information like linear or quadratic main effects or interactions coefficients of the process parameters.

Results and discussion. By using a combination of a two-level full factorial and a face-centered central composite design, the volume flow has been shown to have only minor relevance under the chosen settings. The temperature of the heating mantle also has limited influence on the laughing gas selectivities and mainly serves to support the quasi-adiabatic conditions of the setup. The remaining three parameters are the same that are varied in industrial setups and further validates the system. Additionally, the quadratic and interaction effects of the parameters could be described for the first time. This includes derived parameters like the partial pressure of ammonia, the nitrogen loading, the adiabatic temperature increase and more.

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OFMSW as a potential secondary raw material for chemical recycling

J. Bobek-Nagy[1], E. Tóth*[1], R. Fejes[1], K.Berta[1],A. Sarkady R[1]. Kurdi[1]
1 Sustainability Solutions Research Lab, University of Pannonia, Veszprém, Hungary
*toth.eliza@mk.uni-pannon.hu

Keywords: OFMSW, plastic waste, chemical recycling, circular economy

Introduction. Municipal solid waste (MSW) management is crucial from the aspect of the environment, sustainability, and circular economy. In Europe, the MSW is generally handled in a Mechanical-Biological Treatment (MBT) plant. At the beginning of the process, the organic fraction (OFMSW) is mechanically sorted from MSW (usually <5-8 cm) [1]. The OFMSW can be counted as 40-85 % depending on the seasonality and location of the MSW such as developing or developed countries [2]. The OFMSW is commonly treated by biostabilization which means a 3-4 weeks long aerobic biological processing after that, the remaining material is directed to the landfill [3]. Accordingly, that way of the process does not fit the circular economy approach and moreover does not comply with the EU Landfill Directive of April 1999 (99/31/EC) furthermore the directive forces the decline of the total amount of deposited household waste under 10 % by 2035 (without derogation) [4,5]. According to the significant ratio (7-23 %) [6] of plastic in OFMSW, the plastic part can be a potential raw material for chemical recycling to reach the goal of the circular economy.

Experimental/methodology. OFMSWs were sampled in three different seasons (spring, summer, winter), from the biological fraction (particle size under 6 cm) of a Hungarian, MBT plant with 120 000 tonnes/year household solid waste capacity. The samples were stabilized in our laboratory. After the stabilization process, the particle size and the composition of them were established furthermore the types of the different plastic were determined by FT-IR.

Results and discussion. Investigating the composition of the total batch of OFMSW, the season has no significant effect on the plastic ratio. The quantity of plastic changes between 15 and 17 w/w% under 6 cm. However, in the aspect of plastic rate in different particle size fractions (1-2, 2-4, and 4-6 cm) in OFMSW, the season has more influence on plastic proportion. Over 4 cm, the plastic quantity is less in winter (24 w/w%) while the greatest in summer (42 w/w%). In the 2-4 cm particle size fraction, season indicates a continuous decrease, in spring the plastic rate is 30 w/w%, in summer is 24 w/w%, and in winter is 18 w/w%. Generally, it can be said that the average plastic content over a year is 12 w/w % in 1-2 cm, 24 w/w% in 2-4 cm, and 35 w/w% in 4-6 cm particle size of OFMSW fraction. However, in the aspect of plastic rate in different particle size fractions, In the case of particle size fraction According to the FT-IR measurement the PP and HDPE reach more than 70 w/w% among plastics which is a suitable secondary raw material for chemical recycling.

Acknowledgments
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Structure and Activity Relationship Studies of Double Metal Cyanide Catalyzed Ring-Opening Polymerization of Cyclic Monomers

C. H. Tran, H.-K. Choi, E.-G. Lee, B.-R. Moon, I. Kim*

School of Chemical Engineering, Pusan National University, Busan, Republic of Korea
**ilkim@pusan.ac.kr*

Keywords: double metal cyanide, ring-opening polymerization, polyether, polyester, polycarbonate

Introduction. Prussian blue analogue (PBA) complexes are presentative materials of metal-organic frameworks which are highly crystalline and stablematerials. The crystallinity and crystal structure of PBAs are subjected to change according to the preparations. PBAs with substantially amorphous structures, mostly known as double metal cyanide (DMC) catalysts, are well-established for numerous organic reactions, most notably ring-opening polymerization (ROP) of epoxides, copolymerization of CO_2 with epoxides, and ROP of lactones [1-3]. Thus, understanding of the structure-activity relationship is one of the important step to optimize the overall performance of this catalytic system.

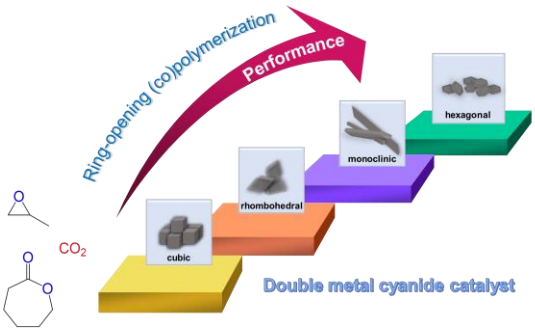

Figure 1. Illustration of the influence of morphology on activity of DMC catalysts.

Experimental/methodology. DMC catalysts of cubic, rhomboheral, monoclinic, hexagonal, and amorphous structure were prepared by modifying parameters such as temperature, precipitation method, and the use of organic additives or templates. The compositions and structural properties of the catalysts were determined by inductively coupled plasma optical emission spectrometer, elemental analysis, thermogravimetric analysis, X-ray powder diffraction (XRD), and scanning electron microscope (SEM). Indexing, Pawley fitting and Rietveld refinement of the powder diffraction data were performed using the Fullprof suit software. The textural properties of the catalyst were analyzed by N_2 sorption isotherms using Brunauer-Emmett-Teller method. The density functional theory (DFT) calculations were performed using BIOVIA Materials Studio 2020 (20.1)

Results and discussion. A series of Zn-Co DMC catalysts having a range of crystal structures have been investigated for the ring-opening polymerization of propylene oxide, ε-caprolactone, and copolymerization of propylene oxide and CO_2. The XRD patterns, refined by the Rietveld method, and SEM images indicate that DMC catalysts of cubic (c-DMC), rhombohedral (r-DMC), monoclinic (m-DMC), and hexagonal (h-DMC) morphologies with respectively *Fm*-3*m*, *R*-3*c*, $P2_1/m$, and *P*11*m* space groups were successfully fabricated under various conditions. m-DMC and h-DMC exhibit superior activities compared to those of c-DMC and r-DMC catalysts. DFT studies were further conducted to understand the structure-activity relationship.

Acknowledgments

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (2021R1A2C2003685) and was partly supported by a Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korean government (MOTIE) (20208401010080)

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Methanol Oxidation reactions on silver using an annular reactor

Y. van Valen[1*], T. Bergh[1], T. Skrzydlo[1], O.H. Bjørkedal[2], T. By[3], R. Lødeng[4], J. Yang[1], H.J. Venvik[1]

[1]*Norges teknisk-naturvitenskapelige universitet, Trondheim, Norway*
[2]*Dynea AS, Lillestrøm, Norway*
[3]*K.A. Rasmussen, Hamar, Norway*
[4]*SINTEF Industri, Trondheim, Norway*
[*]*youri.van.valen@ntnu.no*

Keywords: Silver, Oxidation, Methanol-to-Formaldehyde, Annular reactor

Introduction. The partial oxidation of methanol to formaldehyde (MTF) over a silver catalyst is an important process for the global formaldehyde production, being responsible for about 55% of the total production. A complex reaction system has been suggested but kinetic investigations to prove the mechanism have been challenging[1, 2]. Lab scale investigations have traditionally resulted in complete conversion of oxygen when running at near industrial conditions. Furthermore, interactions between oxygen and silver and the resulting surface morphology play a role in the activity of the catalyst[3]. An annular reactor concept has been developed and implemented to aid in conducting kinetic investigations. By using a cylindrical silver monolith (Ø 10mm) inside a narrow slit, the reaction can be run using short residence times while limiting the influence of mass transfer and suppressing gas phase reactions[4]. This allows us to conduct the MTF reaction at low conversion, to elucidate the role of different sub-reactions as well as the silver-oxygen dynamics[2].

Experimental/methodology. CO, H_2, and methanol oxidations are performed at industrially relevant temperatures (500-650°C) at atmospheric pressure. Both short- (<12h) and long-term(>80h) experiments are performed to evaluate the influence of the development of the silver surface over time on the activity. Post-experiment analysis of the catalyst to follow the restructuring is done by electron microscopy.

Results and discussion. Using the annular reactor setup a selectivity towards formaldehyde of 93-97% has been reached in the 540 to 600°C range, while maintaining incomplete conversion[2]. A significant effect of surface development over time is observed, as both methanol and oxygen conversion increases. H_2 and CO oxidation show similar trends with activity changing with increased time on stream. Furthermore, post-reaction analysis of the catalyst surface shows that reaction atmosphere has a significant influence on the resulting surface morphology. Hydrogen containing atmospheres show a significantly higher degree of restructuring and pinhole formation.

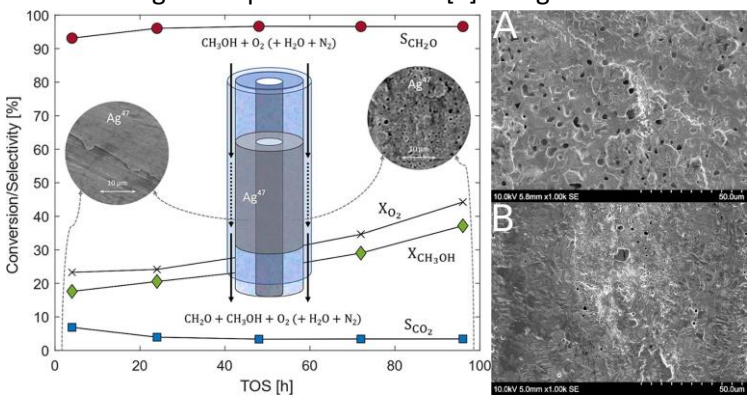

Figure 1: Left: Evolution of conversion, selectivity and annular Ag catalyst surface over time for methanol oxidation. Right: Catalyst surface after (A) H_2 (88h) and (B) CO oxidation (91h)

Acknowledgments

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Natural-polymers-based nanocomposites prepared through ultrasound-assisted hydrosolvothermal methods: Selective photoredox catalysis

Juan Carlos Colmenares*, Behdokht Hashemi, D. Lomot

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
**Corresponding Author's E-mail address: jcarloscolmenares@ichf.edu.pl*

Introduction: This work is a report of recent selected experiments of photocatalysts fabricated by an ultrasound-based technique for photocatalytic selective oxidation of aromatic alcohols (e.g. benzyl alcohol, BnOH), in the frame of the concept of lignin valorization, and the proof of concept of intensifying a flow selective photocatalytic oxidation process by acoustic cavitation.

Experimental/methodology:

A series of chitosan–lignin (CL) composites were prepared through a hydrothermal method by varying the weight ratio of chitosan and lignin. Subsequently, these CL composites were combined with titania (T) to form a nanocomposite (T/CL) using sol–gel and hydrothermal based methods. Additionally, ultrasonication (US)-assisted hydrosolvothermal method was used for the synthesis of metal-free-carbon-based composite photocatalysts. A plethora of parameters that affects the acoustic cavitation phenomena, and as a result the potential of sonication were investigated (e.g. ultrasound frequency and power). Various important photocatalytic parameters such as the wavelength and intensity of the irradiated light, photocatalyst loading, type of solvent, mixture of solvents, and solution pH were also optimized. The synthesized photocatalysts were characterized by using different techniques such as UV-Vis diffuse reflectance spectroscopy, X-ray diffraction, nitrogen sorption, thermal gravimetric analysis and transmission electron microscopy, among others.

Results and discussion:

T/CL nanocomposites exhibited improved photocatalytic performance in comparison with sol–gel and hydrothermally prepared pristine titania (SGH-TiO_2), towards the selective oxidation of benzyl alcohol (BnOH) to benzaldehyde (Bnald) under UV (375 nm) and visible light (515 nm).[1] More specifically, the 75T/CL(25:75) nanocomposite (a representative photocatalyst from the 75T/CL nanocomposite series) showed very high selectivity (94%) towards Bnald at 55% BnOH conversion under UV light. Whereas, SGH-TiO_2 titania exhibited much lower (68%) selectivity for Bnald at similar BnOH conversion. Moreover, the 75T/CL(25:75) nanocomposite also showed excellent Bnald selectivity (100%) at moderate BnOH conversion (19%) under visible light. Whereas, SGH-TiO_2 did not show any activity for BnOH oxidation under visible light. XPS studies suggest that the visible light activity of the 75T/CL(25:75) nanocomposite is possibly related to the doping of nitrogen into titania from chitosan. However, according to UV-visible-DRS results, no direct evidence pertaining to the decrease in band-gap energy of titania was found upon coupling with the CL composite and the visible light activity was attributed to N-doping of titania. Overall, it was found that T/CL nanocomposites enhanced the photocatalytic performance of titania via improved light harvesting and higher selectivity through mediation of active radical species. On the other side, the metal-free carbon-based photocatalysts presented promising activity (30%) and selectivity (>70%) in the partial oxidation of phenolics under flow sonophotocatalytic conditions.[2] The effort of our research is focused on the utilization of flow sonophotocatalysis for the selective transformation of lignin-based model molecules by metal-free carbocatalysts.

Acknowledgments:
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Effect of catalyst composition and preparation method on the activity and stability of Ni-Pt based catalysts for methane steam reforming

A. De Giacinto[1*], E. Tusini[1], M. Casapu[1], D. E. Doronkin[1,2], A. Zimina[2], J.-D. Grunwaldt[1,2*]

[1]Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology, Karlsruhe, Germany. [2]Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany.

**andrea.degiacinto@kit.edu; *grunwaldt@kit.edu*

Introduction

Besides the importance of H_2 as raw material for chemical industry, its role as C-free energy carrier has increased tremendously during recent years. Despite CO_2-neutral sources are desired, H_2 is produced currently at large-scale by reforming of fossil fuels, mainly by methane steam reforming (SR) [1]. A widely used catalyst for this process is Ni/Al_2O_3, with a metal loading ranging between 15-20 wt.% [2]. Alternatively, supports such as $MgO\text{-}Al_2O_3$ mixed oxides or bimetallic catalysts can be used. However, the main drawbacks of all Ni based catalysts are coke deposition and sintering due to the high temperature required for this reaction (up to 900°C). Both deactivation pathways can be hindered by adding small amounts of noble metals like Pt, Pd, Rh to the Ni-based catalyst [3]. In this context, our study aims at understanding the role of Ni-Pt/$MgAlO_x$ catalyst composition and synthesis method on the activity and particularly on catalyst deactivation behavior.

Experimental/methodology

A series of Ni-Pt/$MgAlO_x$-based catalysts with various Ni:Pt:support ratios were prepared by conventional and advanced preparation methods, i.e. flame spray pyrolysis [4]. The resulting samples were characterized by electron microscopy, XRD, H_2-TPR, N_2-physisorption and Raman spectroscopy. Systematic methane SR tests were conducted in a plug-flow reactor for different steam-to-carbon (S:C) ratios. A FTIR spectrometer (Multigas FTIR Spectroscopy, MKS) and a mass spectrometer (Omnistar 320, Pfeiffer) were used for the analysis of the gas mixture at the reactor outlet. The evolution of Pt and Ni structure during methane SR was studied by *operando* X-ray absorption spectroscopy measurements at Pt L_3 and Ni K edges.

Results and discussion

Transmission electron microscopy showed different morphologies of the support depending on the synthesis method. XRD analyses confirmed the synthesis of the desired phases and revealed compositional differences in the as-prepared catalysts according to the Ni and Pt concentrations. In general, a clear impact of the catalyst composition on catalytic performances was found especially during deactivation tests at low S:C ratios. Raman spectroscopy confirmed the presence of graphitic coke for the samples affected by coking. All in all, our findings contribute to the rational development of this class of catalysts based on fundamental understanding.

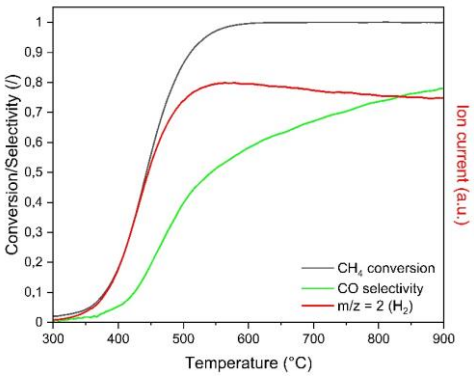

Figure 1: Catalytic activity of a typical Ni-Pt/$MgAlO_x$ catalyst during a temperature ramp (S:C = 3, 6600 ppm CH_4).

Acknowledgments

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Palladium-catalyzed double reductive amination of bisphenols to high value diamines

M. Degelin[1*], S. Van Minnebruggen[1], D.E. De Vos[1]

[1]*centre for membrane separations, adsorption, catalysis and spectroscopy for sustainable solutions (cMACS) KU Leuven, Belgium*

[*]*matthias.degelin@kuleuven.be*

Polyurethane is one of the most prevalent condensation polymers being produced at 18.6Mt scale [1]. This important polymer finds applications in many industries such as automotive, insulation and textiles. An important precursor for this polymer is (hydrogenated-)methylenedianiline ($(H_{12}$-)MDA). However, the majority of this precursor molecule is produced via the condensation of aniline with formaldehyde. Traditionally, the production of aniline is based on the nitration reduction of benzene [2]. Producing large acidic waste streams and starting from fossile resources- e.g. benzene, this multi-step process shows distinct technological disadvantages. Additionally, the poor regioselectivity for the 4,4'-isomer during the acid catalyzed condensation reaction between aniline and formaldehyde further highlights the need for alternative pathways.

In previous works, Cuypers et al. succesfully reported the amination reaction of phenols towards both anilines and cycohexylamines using heterogeneous palladium- and nickel-catalysts respectively [3,4]. Both works proposed a one-step catalytic system obtaining excellent yields and selectivities for the desired primary amines. Nevertheless, the problems of the condensation reaction towards MDA were not solved in these reports. An alternative and more sustainable route to these high value dimamines could be found in the upgrading of bisphenols due to their similar chemical skeleton to (H12-)MDA. Bisphenols are produced on a vast scale for polycarbonate (PC) (4.7 Mt/yr)[4]. Phenol, the starting material of bisphenol, is a cheap greener alternative to aniline to produce MDA. Besides, the condensation reaction of phenols to bisphenols shows an increased 4,4'-isomer preference. Combining the more efficient synthesis of bisphenols with reductive amination improves the overall synthetic pathway of MDA's. Additionally, no clear end-of-life solution is known for PC currently, implying that polycarbonate is either incinterated or landfilled. Efficiently depolymerizing PC back to bisphenols would provide a new feedstock for (H_{12}-)MDA and while revalorizing a plastic waste stream.

In this work, we tackled the listed problems above. Focussing on the heteregeneously catalysed double reductive amination of bisphenols using ammonia and hydrogen-gas as green reagents. A dedicated amination set-up was built in which precise control over the H_2 and NH_3 concentrations in the liquid phase was possible. Both commercially available and self-prepared supported palladium catalysts were assessed. Thourough evaluation of the critical reaction parameters such as H_2- and NH_3-pressure, catalyst support, time and temperature led to excellent yields (>90%) and (>90%) for H12-MDA starting from bisphenol F (BPF). During this research the equilibrium position between the primary and secondary amine was investigated using dicyclohexylamine as a model compound. This concluded that secondary amine formation can not be excluded during reductive amination reactions. Characterisation of the catalysts revealed a structure-sensitivity relationship allowing us to further optimize the catalytic system. Small Pd carticle sizes was of great benefit for the reaction time and improved selectivity for the primary diamine greatly [5,6]. In the final part of this research, the susceptibility for nucleophilic attacks of the carbonate bond was eploited to isolate Bisphenol A (BPA) from polycarbonate (PC). Ammonolysis proved to be a succesful method, efficiently depolymerizing PC to BPA on gram scale (87% isolated yield) generating only urea as a stoichiometric side-product. The virgin as well as the isolated BPA was used in the reductive amination. Both obtained excellent yields, however, their reaction rate were significantly reduced.

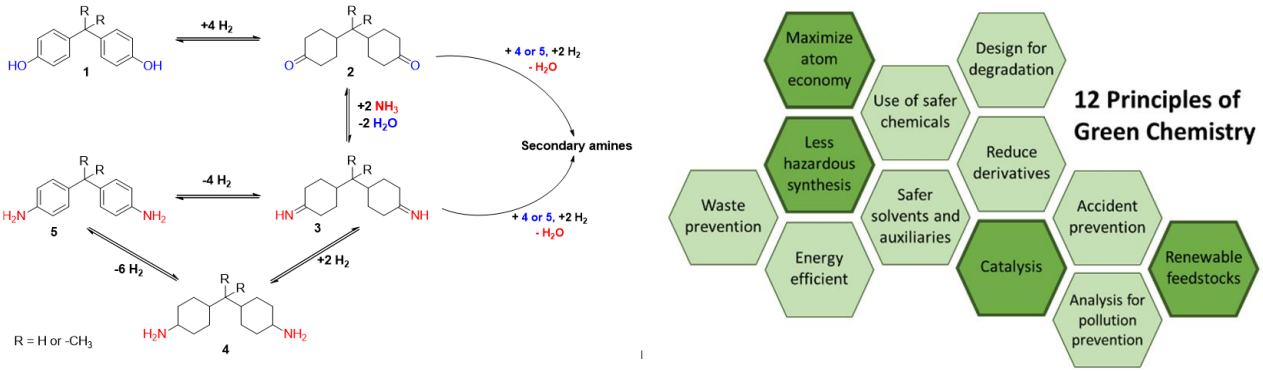

Figure 1: reaction pathway of Bisphenol to (H12-)MDA (left) and the 12 principles of green chemistry (right)

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Active and Regioselective Ru Single-Site Heterogeneous Catalysts for Alpha-Olefin Hydroformylation

Francisco Javier Escobar-Bedia[1], Miguel Lopez-Haro[2], Jose Juan Calvino[3], Vlad Martin-Diaconescu[3], Laura Simonelli[3], Virginia Perez-Dieste[3], Maria J. Sabater[1], Patricia Concepción[1], Avelino Corma[1]*

[1] *Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas (UPV-CSIC), Avenida de los Naranjos s/n, 46022 Valencia, Spain*
[2] *Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Cádiz, Spain*
[3] *CELLS - ALBA Synchrotron Radiation Facility, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallès, Spain*
fraesbe5@itq.upv.es

Keywords: Ruthenium, single-site, regioselectivity, hydroformylation

Introduction.

Olefin hydroformylation is one of the major examples of a homogeneous catalytic process at industrial scale to produce bulk chemicals[1]. Currently the process is carried out using expensive Rh-based catalysts with phosphine ligands[2]. The high cost and low abundance of Rh has made recycling and catalyst recovery key from both the economic and environmental point of view. In response different heterogeneous catalytic systems, mostly using Co and Rh[3], have been developed with limited success due to expensive synthesis or subpar activity/regioselectivity results. As an alternative, we propose a new type of heterogeneous ruthenium catalyst consisting of isolated single atoms and disordered clusters stabilized in a mesoporous N-doped carbon matrix with very good activity and remarkable regioselectivity (up to 92%) towards the production of n-heptanal from 1-hexene.

Experimental/methodology.

The catalytic tests were performed using a stainless-steel autoclave fitted with a PEEK (poly- ether-ether-ketone) liner at 150 °C and 40 bar of syngas pressure ($CO:H_2$ = 1:1). The reactor was equipped with temperature and pressure control and the reaction mixture was stirred magnetically. The extraction of liquids at high pressure was carried out through a gas-tight syringe. A 250 µL gas-tight Hamilton syringe was used to extract 25 µL aliquots at different reaction times.

Results and discussion.

Several catalysts were synthesized varying the Ru loading, from 0.01% wt. to 0.4% wt., and tested in the hydroformylation of 1-hexene. A significant increase of the catalytic activity could be noticed by decreasing the metal loading (Figure 1). A priori, these results indicate a strong relationship between the catalytic activity and the size of these Ru entities. The structure-activity relationship of the Ru species was further studied by means of Aberration Corrected Electron Microscopy, revealing the presence of uniformly distributed Ru single atoms (SAs) in samples with low loading, low atomicity clusters for intermediate loadings and bigger agglomerates at high loadings (Figure 2). By combining the catalytic experiments with the observed HAADF-STEM particle distribution, it is possible to determine de intrinsic activity for each Ru entity, hence assigning the remarkable activity observed at low loadings to SAs, whereas the lowest activity to formation of larger size agglomerates such as medium size clusters and nanoparticles.

Next, to check the re-usability of the catalyst, two samples with 0.01% and 0.2% wt. Ru were subjected to 4 consecutive reaction cycles (Figure 3) in which only a small decrease in the activity parameters (TON, TOF) can be noted, though selectivity towards 1-heptanal is maintained during all recycles for both catalysts. Finally, the effect of the α-olefin chain length was analysed, obtaining in all cases similar results as with 1-hexene.

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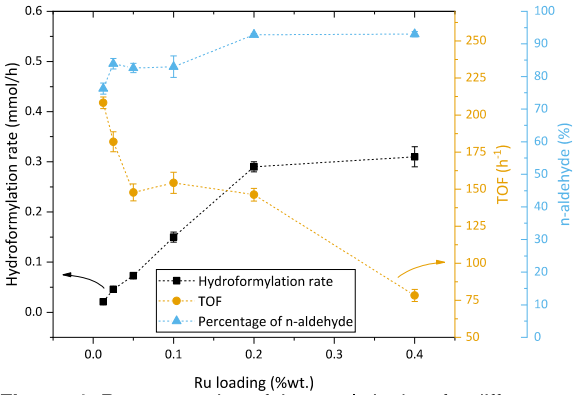

Figure. 1. Representation of the catalytic data for different Ru@NC loaded catalyst: Hydroformylation rate, black (left); Turn over Frequency (TOF), orange (assuming all metal entities are active) and n-heptanal selectivity, blue (right).

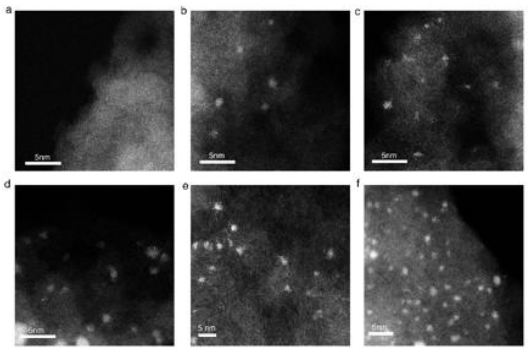

Figure 2. Aberration-corrected HAADF-STEM images for (a)0.0125Ru@NC, (b) 0.025Ru@NC, (c) 0.05Ru@NC, (d) 0.1Ru@NC and (e) 0.2Ru@NC and (f) 0.4%Ru@NC.

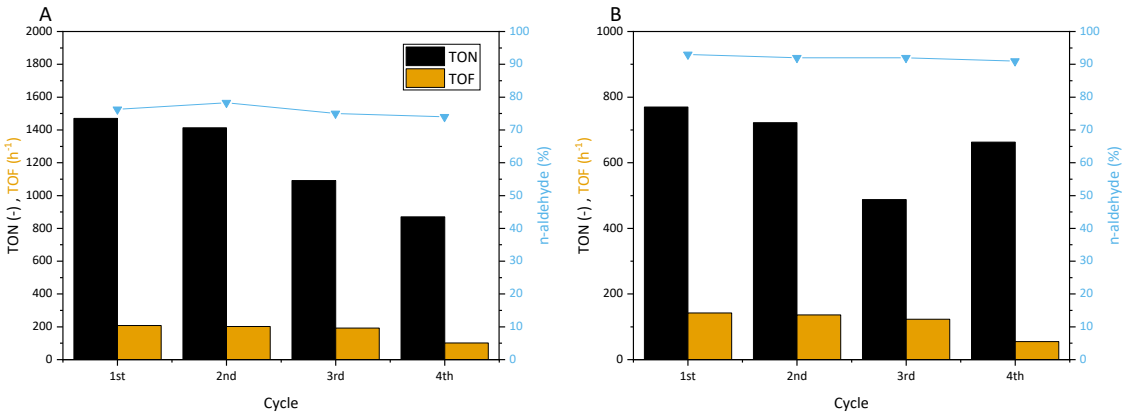

Figure 3. Representation of the most important catalytic data for each re-use of A) 0.0125Ru@NC and B) 0.2Ru@NC catalysts. TON and TOF are calculated based on all metal equal active.

Methyl Acetate production over cation exchange resin catalysts

N.S Govender[1*], J. Miranda[1], R. Balasubramanian[1], S. B Mamilla[1]

[1]*Sahara International Petrochemical Company, Jubail, Saudi Arabia*
[*]*ngovender@sipchem.com*

Keywords: Methyl aceate, methanol, acetic acid, resin catalyst, esterification

Introduction. The esterification of acetic acid with methanol to produce methyl acetate can be catalysed with either homogeneous or heterogenous catalysts (1). Homogeneous catalysts are preferred commercially mainly due to their higher activity. However, these catalysts have a higher corrosive nature, result in more side reactions, and are difficult to separate from the reaction medium. For these reasons, heterogeneous catalysts such as cation exchange resins are considered as attractive alternatives, as they potentially offer less of these undesirable features. In this present work, we demonstrate a scaled-up process for methyl acetate production by reactive distillation catalysed by a cation exchange resin. We also present here the laboratory development work prior to scale-up.

Experimental/methodology. Six different cation resin catalysts were tested with sulphuric acid being the reference catalyst. Initial screening tests were performed on batch reactors at 60 °C for 90 min with stirrer speed set to 500 rpm. Gas chromatography was used to determine the acetic acid conversions. A reflux setup (2) was used to measure the esterfication kinetics by changing the catalyst loadings, feed ratios, and reaction temperature. These results were then used to design the scale-up experiments.

Results and discussion. The laboratory experimental tests on different cation resin catalysts showed varying activities compared to the reference sulfuric acid catalyst. The most active resin catalyst tested showed 80 % relative activity to sulfuric acid (see Figure 1). The other reaction parameters tested (catalyst loadings, feed ratios, and temperature) gave valuable insights into the performance of this resin relative to sulfuric acid. Overall, the kinetic response of the resin is slower than sulfuric acid thus making direct replacement in existing equipment more challenging. A scale-up pilot study using a reactive distillation column will provide more detailed kinetics and show the robustness of the resin catalyst under these conditions.

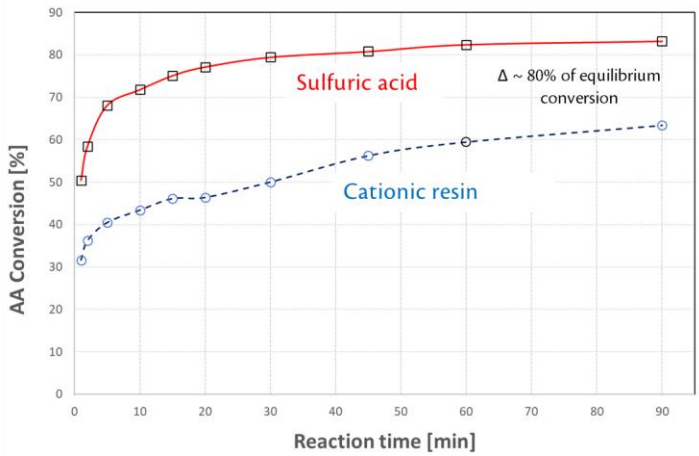

Figure 1. Acetic acid conversion versus time for the esterification with methanol catalyzed by (☐) 1g H_2SO_4 and (○) 1 g Thermax Tulsion T-6812MP resin. Reaction conditions: 60 °C with feed mole ratio = 1.

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Sustainable synthesis of silicon precursors coupled with hydrogen delivery based on circular economy via cobalt-based catalyst

Silvia Gutiérrez-Tarriño,[1] Sergio Rojas-Buzo,[1,2] Manuel A. Ortuño[3] and Pascual Oña-Burgos[1]

[1]*Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas (UPV-CSIC), Avda. de los Naranjos s/n, 46022 Valencia, Spain.*
[2]*Department of Chemistry, NIS and INSTM Reference Centre, Università di Torino, 10125, Italy.*
[3]*Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.*
[*]*silgutar@doctor.upv.es*

Keywords: hydrogen delivery, green hydrogen, alkene hydrosilylation, dehydrogenative coupling, cobalt complex, homogeneous catalysis.

Introduction.
The development of a circular economy is a key target to reduce our dependence on fossil fuels and create more sustainable processes. Concerning hydrogen as energy vector, the use of liquid organic hydrogen carriers is a promising strategy.[1] However, most of them present limitations for hydrogen release, such as harsh reaction conditions, poor recyclability, and low-value by-products.

Results and discussion.
A novel sustainable methodology to produce added-value silicon precursors and concomitant hydrogen via dehydrogenative coupling by using an air- and water-stable cobalt-based catalyst synthesized from cheap and commercially available starting materials has been developed.[2] This methodology is applied to the one-pot synthesis of a wide range of alkoxy-substituted silanes using different hydrosilanes and terminal alkenes as reactants in alcohols as green solvents under mild reaction conditions (room temperature and 0.1 mol% cobalt loading). We also demonstrate that the selectivity toward hydrosilylation/hydroalkoxysilylation can be fully controlled by varying the alcohol:water ratio. This implies the development of a circular approach for hydrosilylation/hydroalkoxysilylation reactions, which is unprecedented in this research field up to date. Kinetic and in situ spectroscopic studies (EPR, NMR, ESI-MS), together with DFT simulations, further provide a detailed mechanistic picture of the dehydrogenative coupling and subsequent hydrosilylation. Finally, we illustrate the application of our catalytic system in the synthesis of an industrially-relevant polymer precursor coupled with the production of green hydrogen on demand (Figure 1).

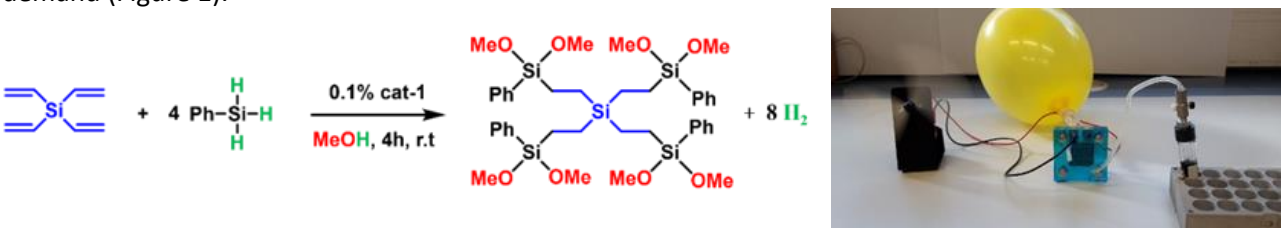

Figure 1. Hydroalkoxysilylation reaction of tetravinylsilane and phenylsilane to obtain a silicon precursor (left) and a picture of energy generation via recombination of hydrogen obtained in the hydroalkoxysilylation reaction and oxygen balloon in a fuel cell (right).

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Utilizing Water-Catalyst Interactions to Stabilize the Transition State During Alkane Dehydrogenation

J.P. Haven[1], L. Lefferts[1], J.A. Faria Albanese[1*]

[1]*Catalytic Processes and Materials, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, the Netherlands*
[*]*j.a.fariaalbanese@utwente.nl*

Keywords: ethane dehydrogenation, platinum, steam

Introduction. Ethylene is a widely used chemical building block that is conventionally produced via cracking processes. A more direct route to produce ethylene is via ethane dehydrogenation (EDH, $C_2H_6 \leftrightarrow C_2H_4 + H_2$, ΔH^0 = +137 kJ/mol). EDH requires high temperatures (500-700 °C), is limited by thermodynamic equilibrium (ethylene yield: ~30%), and is therefore currently not industrially attractive. Ethylene yields can be increased by using H_2 permeable dense ceramic membranes [1]. Co-feeding H_2O (0-5 V%) is known to enhance H_2 permeation through these membranes [1] and is known to improve the lifetime of Pt-based catalysts [2]. Alkane dehydrogenation on Pt catalysts has been widely investigated in the past, but the role of H_2O on the corresponding reaction kinetics is still poorly understood. In this contribution, we will show the effect of H_2O (0-5 V%) on the reaction kinetics of non-oxidative dehydrogenation of ethane using a $Pt/ZnAl_2O_4$ catalyst.

Experimental/methodology. The $ZnAl_2O_4$ support is functionalized with 4.0 wt% Pt via wet impregnation. Catalytic tests were performed in a continuous flow, fixed-bed reactor setup, equipped with a syringe pump to co-supply H_2O. The typical testing conditions were: temperatures of 475-550 °C, atmospheric pressure, 10-150 mbar ethane, 10-150 mbar H_2, 0-15 mbar H_2O. The composition of the reactor outlet was analyzed while performing the reaction using an on-line gas chromatograph.

Results and discussion. The reaction orders in ethane (=1), ethylene, and H_2 (both -0.5) for EDH on $Pt/ZnAl_2O_4$ were determined to be similar under dry and wet conditions, indicating similar reaction mechanisms. The reaction rate constant is determined as a function of temperature for $Pt/ZnAl_2O_4$ in presence and absence of H_2O (***Fig. 1a***). Interestingly, the enthalpy of the transition state is found to be lowered in wet conditions compared to dry conditions (slope proportionality, 85 vs. 120 kJ/mol), indicating stabilization of the transition state at the Pt surface by H_2O. This is schematically visualized in ***Fig. 1b***, illustrating that polar H_2O facilitates the removal of H-atoms from ethane. This happens at the cost of an entropic penalty (***Fig. 1a***, y-intercept proportionality: -154 J/mol.K instead of -113 J/mol.K), as the number of degrees of freedom of the transition state is reduced by this stabilization effect.

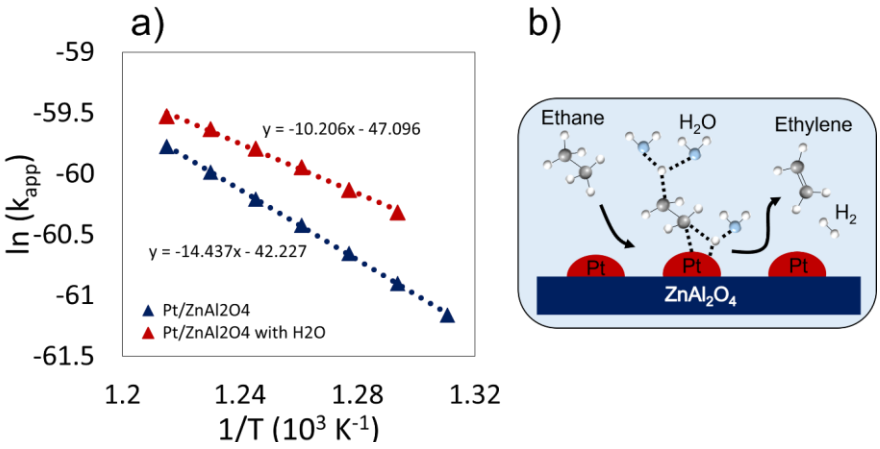

Figure 1: a) Arrhenius curves for ethane dehydrogenation on $Pt/ZnAl_2O_4$ under dry (blue) and wet (red) conditions, T = 490-550 °C, b) schematic of the proposed role of H_2O in the EDH reaction mechanism.

Acknowledgments

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Intermetallic compounds in catalysis

Well-defined active sites in intermetallics: Consequence of nuclearity and composition in selective hydrogenation

G. A Canning[1], K. MacIntosh[1], H. He[1], A. Nguyen[1], M. J. Janik[1], R. M. Rioux[1,2,*]

[1]*Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16801*

[2]*Department of Chemistry, The Pennsylvania State University, University Park, PA 16801*

[*]*rmr189@psu.edu*

Keywords: intermetallics, active site, hydrogenation, kinetics, reaction mechanism

Introduction. Intermetallic compounds, composed of two or more metals, possess long-range crystallographic order (i.e., well defined site occupancy) with distinct differences in catalytic behavior from their parent metals [1]. We demonstrate intermetallic Pd-Zn γ-brass ($Pd_{8+x}Zn_{44-x}$, $0 \leq x \leq 2$) represents an ideal platform to tune the size (nuclearity) and composition of active sites to control selectivity during hydrogenation [2]. Active sites in this system are composed of Pd-M-Pd (M = Zn, Pd, Cu, Au, Ag) units with an angle of 120°. The composition of these PdMPd moieties is controlled by the stoichiometry. Pd_9Zn_{43} (Pd_9) displays a mixture of M = Pd and Zn, while $Pd_{10}Zn_{42}$ (Pd_{10}) only exposes M = Pd. Pd-Pd-Pd sites are unselective for alkyne semi-hydrogenation, while PdZnPd was highly selective towards the olefin. Coinage metals (Cu, Ag, Au) in the system displayed intermediate selectivity. To further explore the active site structure-function relationship, we utilize site isolated Pd-M-Pd (M = Pd, Cu, Ag, Au) trimers to fully elucidate the mechanism of ethylene hydrogenation through combined experimental measurements, density functional theory (DFT) and microkinetic modeling (MKM) [3].

Experimental/methodology. Catalysts are synthesized by a solid-state diffusion technique whereby solid powders of Zn, Pd and either Cu, Ag or Au are physically mixed and heated under vacuum. The resulting bi- or tri-metallic ingot is crushed and then annealed under vacuum to produce the final bulk catalyst. Phase identification and site occupancy is determined by Rietveld refinement of X-ray or neutron diffraction data. The catalytic activity of each material is measured using a plug-flow reactor coupled to a gas chromatograph/mass spectrometer. DFT calculations were performed in VASP to evaluate elementary reaction energetics. Microkinetic modeling was executed by a home-built code. CALPHAD modeling is used to predict the site occupancy and therefore active site composition in the trimetallic case.

Results and discussion. The well-defined active site afforded by the γ-brass phase allows for kinetic models that can accurately describe apparent activation energies and reaction orders for ethylene hydrogenation. Previous studies of the kinetics of ethylene hydrogenation on late transition metal surfaces have required the use of a "special" site on which H can adsorb without competition from ethylene within a Langmuir-Hinshelwood framework. The molecular level definition of such sites is elusive, arising from the complex combination of mixed coverages and differences in adsorbate size between ethylene and hydrogen. The isolation of Pd_1 and Pd_3 sites allows us to provide a precise definition of all possible ethylene-hydrogen co-adsorption structures and hydrogenation reaction paths, enabling a precise definition of site requirements. The high sensitivity of the H_2 reaction order on monomer-and trimer-containing Pd_9Zn_{43} surfaces is due to the significant influence of Pd monomers on the degree of rate control due to competitive adsorption of ethylene and hydrogen on the monomers. This competition decreases at higher temperature as the ethylene coverage decreases on the monomer, leading to a decrease in the H_2 order. This sensitivity disappears on trimer-only containing $Pd_{10}Zn_{42}$ surfaces. The incorporation of a coinage metal (Cu, Ag, Au) into the central atom of the trimer site has distinct kinetic consequences on the kinetics of ethylene hydrogenation. Contrary to Pd_9, the Pd_8Cu_1 reaction orders show non-monotonic behavior with respect to temperature. The increased barrier of H_2 adsorption and dissociation on Cu versus Pd, hydrogen dissociation on Pd-Zn-Pd edge atoms increases the kinetic significance relative to Pd-Cu-Pd trimers, especially at low temperatures.

Acknowledgments

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Design of Multimetallic Alloys Highly Efficient for Oxidative Dehydrogenation of Propane Using CO_2

S. Furukawa[1*], F. Xing[1]

[1] *Institute for Catalysis, Hokkaido University, Sapporo, Japan*
[*] *furukawa@cat.hokudai.ac.jp*

Keywords: CO_2, propane dehydrogenation, carbon neutral, intermetallics, high-entropy

Introduction. The oxidative dehydrogenation of propane using CO_2 (CO_2-ODP) is a promising technique for high-yield propylene production and CO_2 utilization. The development of a highly efficient catalyst for CO_2-ODP is of great interest and benefit to the chemical industry as well as net zero emissions. Here, we report unique catalyst materials and design concepts based on pseudo-binary alloys [1] and high-entropy intermetallics [2] for this challenging chemistry. A pseudo-binary alloy is a ternary alloy in which a part of A(B) site in a binary intermetallic A_mB_n is substituted with a third element A'(B') to form $(A_{1-x}A'_x)_mB_n$ ($A_m(B_{1-p}B'_p)_n$) (Figure 1a). Introducing an appropriate third element allows to flexibly tune and improve the catalytic performance, particularly for reactions involving more than one molecules that have quite different properties such as light alakne and CO_2. Futher multimetallization of the A and B sites forms a high-entropy intermetallic $(A_{1-x-y}A'_xA''_y)_m(B_{1-p-q}B'_pB''_q)_n$, which exhibits much greater thermal stability in the high-temperatrue reaction due to entropy effects (Figure 1b).

Experimental/methodology. All the catalysts were prepared by a simple co-impregnation method using CeO_2 (JRC-CEO-2, S_{BET} = 123.1 m^2g^{-1}) as a support. CO_2-ODP was performed in a quartz fixed-bed reactor with a 6 mm internal diameter at 550 °C or 600 °C (C_3H_8: CO_2: He = 1:1:2, a total flow rate of 20 mL/min).

Results and discussion. In this study, we designed $(Pt_{1-x}Co_x)_2In_3/CeO_2$, in which Pt, Co, In, and CeO_2 were chosen for facile C-H scission, CO_2 activation, inhibiting side reaction (ensemble effect), and coke combustion (oxygen releasing ability of CeO_2). HAADF-STEM-EDX, XRD, and XAFS analyses confirmed the formation of nanoparticulate pseudo-binary alloy (x = 0.33) on CeO_2. This catalyst showed high catalytic activity and stability in CO_2-ODP at 550 °C compared with the corresponding monometallic Pt and Pt-based binary alloy catalysts (Figure 1c) [1]. The specific activity of $(Pt_{0.67}Co_{0.33})_2In_3/CeO_2$ was five times higher than that of the best catalyst ever reported, even with a long catalyst life (Figure 1d). However, the stability of this catalyst was not satisfactorily high at 600 °C due to irreversible sintering of alloy nanoparticles. Therefore, we then designed (PtCoNi)(SnInGa)/CeO_2 high-entropy intermetallic catalyst. This catalyst exhibited much longer catalyst life in CO_2-ODP at 600 °C due to greater thermal stability [2]. In the presentation, we discuss about the structural analysis, reaction mechanism, and the roles of each metals in detail.

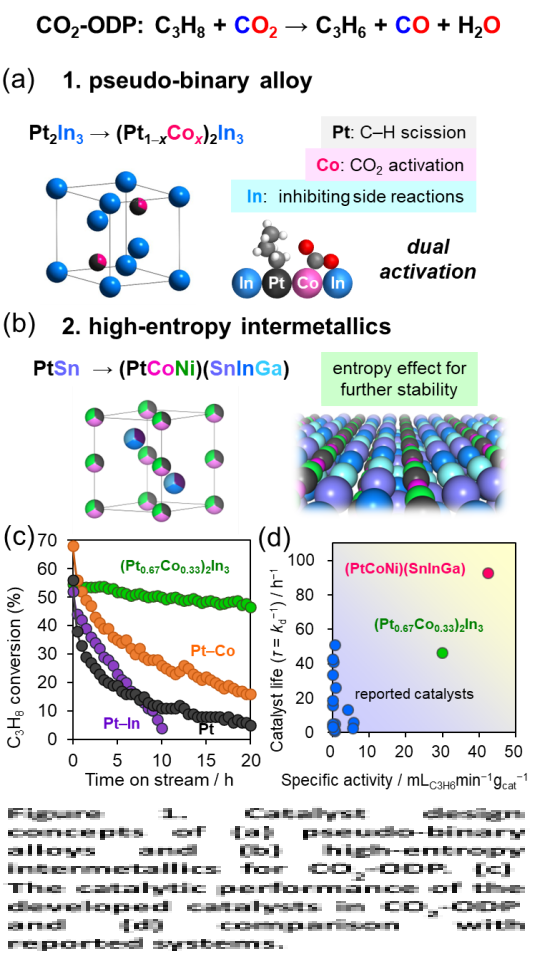

Figure 1. Catalyst design concepts of (a) pseudo-binary alloys and (b) high-entropy intermetallics for CO_2-ODP. (c) The catalytic performance of the developed catalysts in CO_2-ODP and (d) comparison with reported systems.

Acknowledgments

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Relationship between Structure and Catalytic Reactivity of Silica Supported Ni-Ga Nanoparticles for the Hydrogenation of CO_2 to Methanol

N. K. Zimmerli[1], P. M. Abdala[1*], C. M. Müller[1*]

[1]*Department of Mechanical and Process Engineering, ETH Zürich, Zürich, Switzerland*
[*]*abdalap@ethz.ch, muelchri@ethz.ch*

Keywords: bimetallic catalysts, structure-performance, CO_2 hydrogenation, in-situ, operando

Introduction. Many industrially relevant catalysts have active sites that contain more than one metal species [1]. However, even in well-established systems, such as the commercial Cu-Zn(O)-based methanol synthesis catalyst, structure-performance relationships remain debated [2]. In this study, we focused on the detailed characterization of Ni-Ga-based catalysts for the hydrogenation of CO_2 to methanol [3]. The use of in-situ and operando experimentation allowed us to describe its phase, short-range order, electronic structure and surface under relevant conditions (20 bar CO_2:N_2:H_2 = 1:1:3, 230°C) and correlate these with catalytic performance.

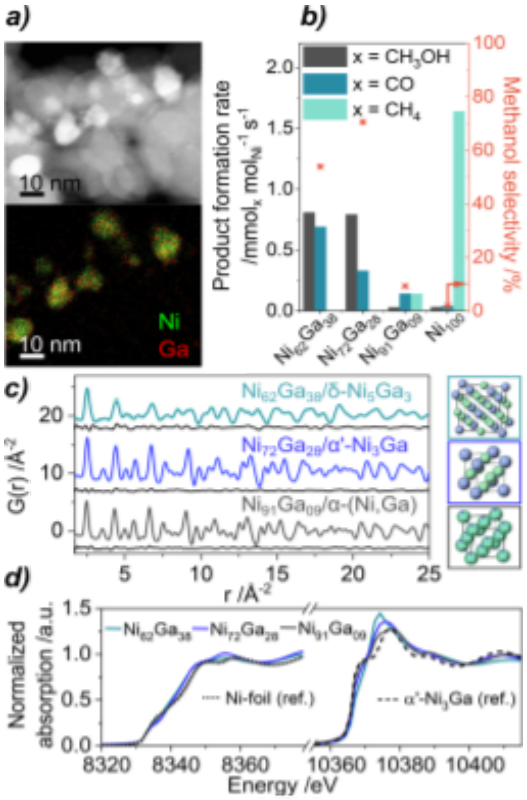

*Figure SEQ Figure * ARABIC 1* **a)** Electron microscopy images of $Ni_{60}Ga_{40}$, **b)** Product formation rate and selectivity, **c)** d-PDF with fitted model structures, **d)** Ni and Ga K edge XANES of Ni-Ga catalysts and reference materials.

Experimental/methodology. SiO_2 supported Ni-Ga catalysts (~ 5 wt% Ni+Ga) were prepared via the hydrothermal deposition precipitation of Ni and Ga nitrate onto colloidal SiO_2 and a subsequent reduction treatment (700°C, 10% H_2/N_2), yielding the as-reduced materials denoted as $Ni_xGa_{(100-x)}$ (x by ICP-OES). Catalytic CO_2 hydrogenation tests were performed in a fixed bed flow reactor (25 bar CO_2:N_2:H_2 = 1:1:3, 230°C, GHSV = 60 L g_{cat}^{-1} h^{-1}) after a pretreatment in H_2 (700°C). Operando X-ray total scattering and operando X-ray absorption spectroscopy experiments were performed at the European Synchrotron Radiation Facility (ID15A and BM31). Difference pair distribution function analysis (d-PDF) of the X-ray total scattering data was determined as d-PDF = $PDF_{Ni\text{-}Ga/SiO2}$ - PDF_{SiO2}.

Results and discussion. Electron microscopy imaging indicated the formation of Ni-Ga nanoparticles of ca. 10 nm Ø (Fig. 1a). Catalytic CO_2 hydrogenation tests revealed a strong dependence of the methanol formation rate and methanol selectivity on the Ni:Ga ratio (Fig. 1b), whereas both $Ni_{62}Ga_{38}$ and $Ni_{72}Ga_{28}$ showed high activities (both ~ 0.8 mol_{CH3OH} mol_{Ni}^{-1} s^{-1}) and selectivities (~ 54% and 70%, respectively). D-PDF of $Ni_xGa_{(100-x)}$ (Fig. 1c) revealed the presence of the intermetallic δ-Ni_5Ga_3 ($Ni_{62}Ga_{38}$) and α'-Ni_3Ga ($Ni_{72}Ga_{28}$) phases in these catalysts under reaction conditions, whereas the poor-performing $Ni_{91}Ga_{09}$ catalyst contained a Ni-rich α-(Ni,Ga) alloy. X-ray absorption near edge structures (XANES, Fig. 1d) indicate that Ni is in a fully reduced $Ni^{0/\delta-}$state and Ga is mostly in reduced state, with only a small fraction of Ga being present in the form of oxidized species; the fraction of oxidized Ga species increases in the following order: $Ni_{62}Ga_{38}$ > $Ni_{72}Ga_{28}$ > $Ni_{91}Ga_{09}$. In summary, our results indicate that the intermetallic δ-Ni_5Ga_3 and α'-Ni_3Ga phases are highly active for the hydrogenation of CO_2 to methanol, whereas a Ni-rich α-(Ni,Ga) alloy is a poor catalyst for this reaction.

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Mars-van-Krevelen Mechanism Revealed for Methanol Steam Reforming over Intermetallic In-Pt/In_2O_3

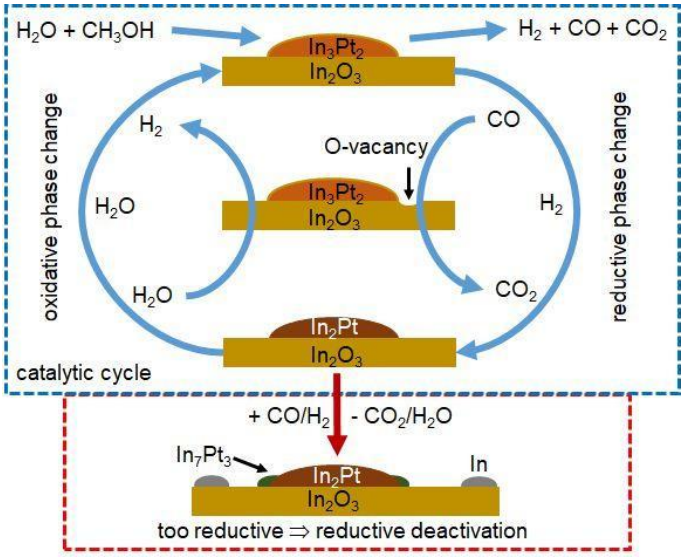
M. Armbrüster[1*], N. Köwitsch[1], L. Thoni[2], B. Klemmed[2], A. Benad[2], P. Paciok[3], M. Heggen[3], A. Eychmüller[2]

[1]*Chemnitz University of Technology, Chemnitz, Germany*
[2]*Dresden University of Technology, Dresden, Germany*
[3]*Ernst Ruska-Centrum, Forschungszentrum Jülich, Jülich, Germany*
[*]*e-mail: marc.armbruester@chemie.tu-chemnitz.de*

Keywords: intermetallic compounds, hydrogen generation, isotope labelling

Introduction. Due to its high energy density, methanol is a feasible substitute for conventional fuels and can be used for on-board hydrogen production for mobile applications.[1] To release hydrogen-on-demand with high purity, methanol steam reforming (MSR, $CH_3OH + H_2O \rightarrow CO_2 + 3\ H_2$) is a well-suited reaction. The most promising catalytic materials are based upon intermetallic compounds of palladium or platinum and have been discovered by Iwasa.[2] While a beneficial effect of the intermetallic compound and the support was detected in the case of ZnPd/ZnO,[3] the underlying reasons for the teamwork are unknown. As intermetallic Pt-In/In_2O_3 has revealed even better catalytic properties in the reaction, this study explores the reasons for the superior activity and selectivity.

Experimental/methodology. Pt/In_2O_3 materials were synthesized by an aerogel route and subsequently turned into Pt-In/In_2O_3 by controlled reductive treatment in hydrogen atmosphere. After characterisation by XRD, DTA/TG/MS and TEM, the materials were tested in methanol steam reforming at varying water-to-methanol-ratios. Mechanistic studies were conducted using ^{18}O-labelled water and methanol in sequence.



Results and discussion. After synthesis, the material consisted of In_3Pt_2/In_2O_3 which changed under reaction conditions and depending upon the water methanol ratio to In_2Pt/In_2O_3 or In_2Pt-In_7Pt_3/In_2O_3.[4] This revealed a highly mobile and redox-active material which adjusts quickly to the reaction conditions. This was further corroborated by experiments using isotope-labelled reactants, which reveal an oxygen-reservoir function of the oxidic support, thus providing strong indications of a Mars-van-Krevelen mechanism. Since this also has been shown for In-Pd/In_2O_3,[5] it is likely that the same principle is applying generally for methanol steam reforming on supported intermetallic compounds.

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Synthesis of Intermetallic Ni-Zn and Ni-Te Nanoparticles by the VapourSolid Synthesis Approach for Heterogeneous Catalysis

D. Garstenauer[1,2*], K. W. Richter[1,3]

[1]*Department of Inorganic Chemistry – functional materials, Faculty of Chemistry, University of Vienna, Vienna, Austria*
[2]*Vienna Doctoral School in Chemistry (DosChem), University of Vienna, Vienna, Austria*
[3]*X-ray Structure Analysis Centre, Faculty of Chemistry, University of Vienna, Austria*
[*]*daniel.garstenauer@univie.ac.at*

Keywords: intermetallic, nanoparticles, heterogeneous catalysis

Introduction

Development and research of sustainable alternatives for energy utilization is mandatory to deal with the challenges of a steadily increasing demand for enery and associated effects on the climate. Key reactions of sustainable energy utilisation include water splitting and steam reforming reactions. Hence, the optimization and development of catalyst materials for respective key reactions play a vital role in current research.[1]

Intermetallic nanoparticles possess unique chemical and physical properties, which make them particularly interesting for catalytic applications. The utilization and synthesis optimization for nanoparticulate intermetallic compounds gained increased attention in recent years. The adjustability of intermetallic materials promises high potential in a variety of heterogeneous catalysed reactions.[2]

State of the art synthesis approaches often lack flexibility and precise composition control while significantly expand particle size distributions, hindering the broad application of intermetallic nanoparticles in catalysis.[3]

Experimental/methodology

A very promising alternative method is the direct vapour solid synthesis of intermetallic nanoparticles by interaction of a metal with high vapour pressure in the gaseous phase with solid metal nanoparticles. In principle, the reaction is driven through the equilibration of a solid component with the vapour of a volatile element. The thermodynamic activity, vapour pressure and thus the product composition are controlled by the reaction temperatures in a temperature gradient.

Results and discussion

In a present approach, we performed the vapour-solid method to prepare various, intermetallic phases as supported Ni-Zn and Ni-Te nanoparticles. Investigation of the samples was carried out by SEM-EDX, TEM, powder XRD, tXRF and gas adsorption. The synthesis method was suitable for producing homogeneous intermetallic compounds of precise and predictable composition. The vapoursolid synthesis is a promising method for the preparation of nanoparticulate intermetallic catalysts. Further metal reactants of interest are the volatile elements Selenium, Antimony and Phosphorus in combination with Nickel, Cobalt, Iron, Gold, Iridium, Platinum, Palladium, Ruthenium and Rhodium. Characterization includes testing of the synthesized nanoparticles in various heterogeneous catalytic reactions. Particularly, water splitting and steam reforming reactions are of interest for investigation.

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Ruthenium Single Atom on Intermetallic Pd_3Pb Nanowires for Highly Efficient Hydrogen Evolution Reaction

Dian Tri Lestarini[1], Ohryeong Suh, and Jong Wook Hong[*]

[1,*]Department of Chemistry, *University of Ulsan, Ulsan, South Korea*
[*]*E-mail address: jwhong@ulsan.ac.kr*

Keywords: Single atom catalysts, Intermetallic compound, Nanowires, Hydrogen evolution, Electrocatalysis

Introduction. The production of alternative hydrogen energy is considered to be a promising way due to its inherent qualities, such as clean, having a high energy density, being affordable, and being a sustainable method. The hydrogen evolution process (HER) in an alkaline medium is one of the practical techniques for the generation of hydrogen due to the significant amount of water electrolysis produced. In particular, Ru-based electrocatalysts have drawn much attention as a benchmark for HER because of their low cost, ability to decrease the reaction barrier of the rate-determining step by weakening the hydrogen-binding energy, and promotion of OH adsorption during HER. Various types of support for anchoring Ru single atoms (SAs) have been widely reported in recent years. Nevertheless, intermetallic nanocrystals (NCs) have yet to be explored among the various supports. Moreover, intermetallic NCs have been shown to have fascinating features due to their ordered atomic arrangement, which is generally more stable in preventing etching during electrocatalytic processes. In this work, we prepared $RuSA_x$-Pd_3Pb NWs via a facile method. The prepared $RuSA_{1.73}$–Pd_3Pb NWs delivered a lower overpotential and Tafel slope than their counterparts. By shedding light on the function of Ru single atom tailoring in intermetallic Pd_3Pb NWs, this study paves the way for developing novel electrocatalysts with increased activity and stability.

Experimental/methodology. First, the intermetallic Pd_3Pb NWs were synthesized via a facile route. In the process of forming intermetallic Pd_3Pb NWs, there was an obstacle in which the nanocubes also produced. Then, the separation method was applied through several steps to increase the yield of nanowires. After the separation method, the ruthenium precursor was added to the organic mixture containing Pd_3Pb NWs. For comparison, Pd_3Pb nanocubes and $RuSA_{2.90}$-Pd_3Pb nanocubes were prepared.

Results and discussion. We have successfully prepared Ru single atom on intermetallic Pd_3Pb NWs through a facile route. The HAADF-STEM images display an ordered atomic structure of Pd_3Pb without any defect after the addition of Ru atoms, confirming the stability structure of the intermetallic phase. Furthermore, the elemental mapping of $RuSA_{1.73}$-Pd_3Pb NWs demonstrates the Ru atoms are atomically dispersed, and no cluster or particles can be found. From ICP-OES measurement, the ratio of Pd/Pb/Ru of $RuSA_{1.73}$-Pd_3Pb NWs was 71.28/26.88/1.73. In addition, the XRD pattern of $RuSA_{1.73}$-Pd_3Pb NWs and Pd_3Pb NWs exhibited diffraction peaks corresponding to the intermetallic Pd_3Pb phase. The XPS survey spectrum confirmed the presence of the Ru element, and the result indicated that Ru received the electron from the Pd_3Pb substrate. The electrocatalytic HER performances of catalysts were evaluated in a typical three-electrode system with N_2-saturated 1.0 M KOH as the electrolyte. The overpotential of $RuSA_{1.73}$-Pd_3Pb NWs is 26 mV at 10 mA cm^{-2}, 10 mV, and 68 mV lower than that of Pt/C and Ru/C, respectively. The Tafel slope of $RuSA_{1.73}$-Pd_3Pb is 40 mV dec^{-1}, indicating the rate-limiting step is the recombination of chemical-adsorbed hydrogen and the HER over the catalysts following the Volmer-Heyrovsky mechanism. In addition, after the long-term stability test, the $RuSA_{1.73}$-Pd_3Pb NWs exhibited excellent durability without any significant losses in potential. These results underlined that an appropriate amount of Ru dispersed on the surface of catalysts could accelerate electron transfer and water dissociation process, which maintain the active sites to alleviate the poisoning of OH_{ads} on the Ru site.

Ga-Sb-Pd Intermetallic Compounds as Catalysts in Semi-Hydrogenation of Acetylene

Kaartick Sivakumar[1], Yuri Grin[2], Marc Armbrüster[1*]

[1]*Chemnitz University of Technology, Chemnitz, Germany*
[2]*Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany*
[*]*Email: marc.armbruester@chemie.tu-chemnitz.de*

Introduction. Semi-hydrogenation of acetylene is an important industrial process to remove traces of acetylene from the ethylene feed used to produce polyethylene.[1] Ga-Pd intermetallic compounds have been studied as catalysts in the semi-hydrogenation of acetylene and were found to exhibit high selectivities and high stability.[2] Substitution of gallium with another main-group element having a higher number of valence electrons results in compounds with different valence electron concentrations, thus the electronic influences in the semi-hydrogenation of acetylene can be studied. An example of this is the catalytic investigation on $Ga_{1-x}Sn_xPd_2$ ($0 \leq x \leq 1$), where the maximum activity was observed at $x = 0.28$.[3] In this work, Ga (with three valence electrons) is replaced with Sb (five valence electrons) to reduce the substitution degree while still improving the activity. Intermetallic compounds $Ga_{1-x}Sb_xPd_2$ ($0 \leq x \leq 0.2$) were synthesised, characterized and catalytically tested in the semi-hydrogenation of acetylene.

Experimental. Intermetallic compounds $Ga_{1-x}Sb_xPd_2$ (x = 0, 0.02, 0.03, 0.035, 0.04, 0.05, 0.1 ,0.15, 0.2) were synthesised in a high-frequency furnace and subsequently enclosed in evacuated quartz glass ampoules before being annealed at 900 °C for three weeks in a resistance oven. Samples were then characterized using metallography and powder X-ray diffraction. This was followed by catalytic tests on crushed samples in a quartz glass tube reactor (plug-flow type) using a gas phase composed of 0.5% C_2H_2, 5% H_2, 50% C_2H_4, 44.5% He at 200 °C and a total flow of 30 mL/min.

Results and discussion. X-ray diffraction as well as metallography resulted in single-phase samples for all compositions. Catalytic testing of these samples revealed that the maximum activity was 16.44 mol_{C2H2} mol_{Pd}^{-1} h^{-1} at x (Sb content) = 0.035. Selectivity towards ethylene was around 80% for all samples. Most samples remained stable throughout the catalytic testing, while slight deactivation can be observed in some samples. The valence electron concentrations (total number of valence electrons divided by total number of atoms) were calculated for the Sb and Sn samples using each atom's valence electron count (Ga =three, Sb = five, Pd = zero, and Sn = 4). Since the valence electron concentration has been doubled for the Sb system compared to the Sn system, the highest catalytic activity should have been observed at half the Sb content (x = 0.14). However, this is not observed and the highest catalytic activity is seen at x = 0.035 (Figure 1). A possible reason for this unexpected behavior could be due to the inert pair effect of Sb, where, similar to Bi, the +3-oxidation state is more stable than the +5-oxidation state.

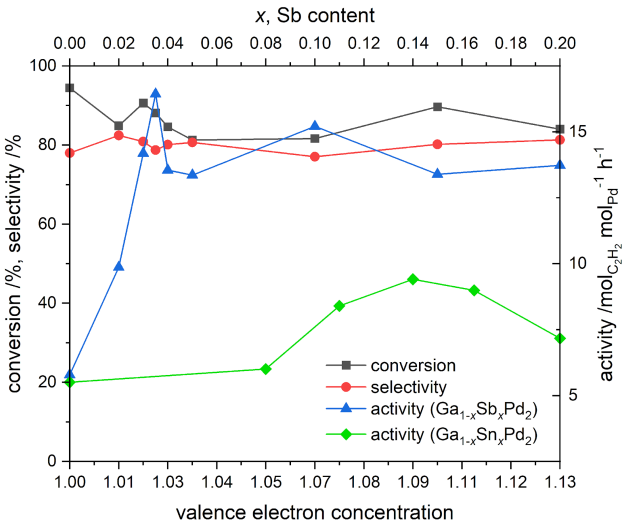

Fig 1. Comparison of conversion, selectivity, activity of the $Ga_{1-x}Sb_xPd_2$ samples, and activity of the $Ga_{1-x}Sn_xPd_2$ samples as a function of x (Sb content) and valence electron concentration

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Photo-driven processes for fuel and organic synthesis

Generation and Utilization of Oxygen Centred Radicals in C–C and C–O Bond Forming Processes

C-J. Wallentin

Gothenburg, Sweden
carl.wallentin@chem.gu.se

Keywords: photocatalysis, radical chemistry

Photocatalytic strategies have shown to not only complement but also expand our ability to achieve structural complexity under mild conditions as compared to methodologies inherently relying on polar mechanisms. Numerous new methods for bond forming transformations have been published in the last decade and the concept of photocatalysis in concert with synergistic catalytic systems have paved the way for innovative approaches for designing complexity generating processes. The generation and utilization of heteroatom centred radicals have lately acquired increased attention from the method development community owing to their useful intrinsic reactivity patterns that can be advantageously utilized in synthesis. However, achieving such high-energy entities in a selective manner under mild conditions is still challenging, and the repertoire of photocatalytic systems that can capitalize on such strategies are still scarce. In the Wallentin group we have developed several methodologies to generate oxygen centred radicals under visible-light mediated conditions and utilized these in various bond forming processes. The talk will cover the latest contribution form the Wallentin group on this topic.

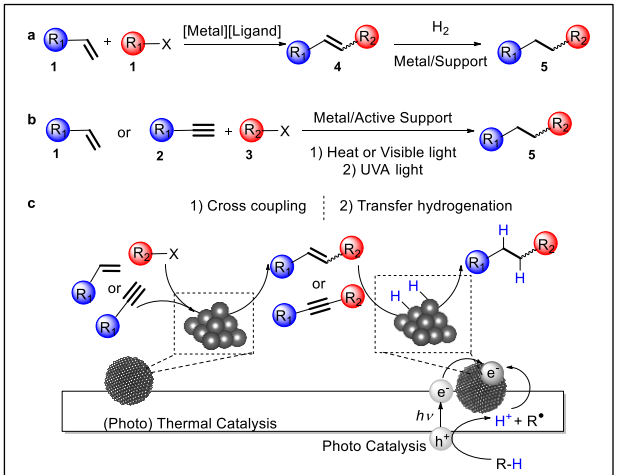
Heterogeneous photocatalysis for sustainable organic transformations: Challenges and opportunities

R. Whitehead, A. Lanterna*

School of Chemistry, University of Nottingham, University Park, NG7 2RD, UK
**anabel.lanterna@nottingham.ac.uk*

Keywords: Photocatalysis, palladium, semiconductors

Introduction. Photocatalysis is a promising technology in the synthesis of fine chemicals and pharmaceuticals allowing the conversion of solar energy into valuable chemicals. Although the widespread application of photocatalysis in industry is yet to be realised, the development of heterogeneous photocatalysts brings promissing advantages over their homogeneous counterparts such as easy separation and potential reusability, which together with the use of light, usually lead to more sustainable processes. Nevertheless, one of the main challenges is to ensure good performance after the first catalytic cycles. Active catalytic species can be inactivated during the catalytic process leading to reduced catalytic efficiency, and with that loss of the advantages of heterogeneous catalysis. We have recently developed an innovative approach to extend catalysts lifetime, 'catalytic farming', based on the crop rotation system used in agriculture.[1] In this innovative approach, different catalytic reactions are performed in sequence using the same catalyst (reaction rotation). As a result, poisoning of the catalyst is prevented because if one reaction depletes certain catalyst properties, they can be restored by another reaction during the next catalytic cycle, thereby extending the catalyst lifetime. However, the approach still relies on multiple separation steps and complete change of reaction conditions between cycles, which limits the sustainability of the process. Here we present our efforts to extend the catalyst lifetime by using the photocatalysts in sequential reactions with minimal changes in the reaction conditions. The catalyst of choice to illustrate this strategy is palladium-decorated titanium dioxide, Pd@TiO_2, is used in sequential catalytic reactions involving organic transformations such as C-C couplings [2] and hydrogenations[3] (Scheme 1).



Scheme 1 | Method design. a. Traditional two-step methodology for formation of new single C-C bonds from cross couplings involving alkenes. **b.** This work approach: sequential cross coupling and transfer hydrogenation reactions triggered by changing irradiation wavelength. **c.** Suggested mechanisms.

Results and discussion. Here we show a sequential photocatalytic method for Sonogashira coupling and transfer hydrogenation reactions is possible, using identical reactions conditions but replacing the irradiation energy. Both, transfer hydrogenations or C-C couplings can be triggered under room temperature and atmospheric pressures and remarkably, the photocatalyst selectivity can be easily tuned by subjecting the reaction to different photon flux. Apparent poisoning of the catalyst is circumbented by filtration of organoiodide species during the first reaction step. The results are rationalised using *in situ* surface analyses (XPS) that suggest changes on the Pd oxidation state are triggered by the presence of the solvent.

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Visible Light Activation of Halogen Bonds Enabled Autocatalytic Intramolecular C(sp^2) - C(sp^2) Coupling of Aryl Sulfonamides

Jaspreet Kaur[1], Mark Mandigma[1,2], Joshua Barham[1*]

[1]*Universität Regensburg, Fakultät für Chemie und Pharmazie, 93040 Regensburg (Germany)*
[2]*University of Bristol, School of Chemistry, BS8 1TS Bristol (United Kingdom)*
[*]*Joshua-Philip.Barham@chemie.uni-regensburg.de*

Keywords: photocatalysis, halogen bond, autocatalysis, biaryl sultams, continuous flow, DFT

Introduction. Cyclic biaryl species are relevant bioactive compounds in medicinal chemistry research and are ubiquitous in pharmaceuticals. Specifically, biaryl sultams (**BASN**) are biologically active compounds and are emerging anticancer species.[1] Classically, biaryls are accessed by expensive transition metal catalysis. Our group explores how non-covalent preassemblies benefit organophotocatalytic system.[2] Thereby, we now report the discovery of a photo-autocatalytic pathway, an efficient process where the product itself acts as a photocatalyst, for the synthesis of **BASN**.

Experimental/methodology. Photochemical batch reactions were carried in a degassed 5 mL crimp vials using 451 nm LEDs. Commercially available Vapourtec R-series was used for scaling up the reaction under continuous flow conditions. Design of Experiments (DoE) was used to optimize the reaction conditions and Gaussian was utilized for the density functional theory (DFT) computational analysis of the reaction mechanism.

Results and discussion. We discovered that **BASN** can be synthesized using visible light without the need of an external photocatalyst (Figure 1). In fact, our computational, kinetic, and other mechanistic studies reveal the slow visible light activation of trialkyl amine – substrate (**1a**) initiates the process, while the accumulation of deprotonated product **2b** (**BASN**) accelerates the reaction which is the key feature of autocatalysis. We have successfully applied the synthesis of various **BASN** (**2b** to **2e**) using flow with decagram per day of productivity, expanding this chemistry's utility for large scale synthesis. We envisage a translational impact from our research to other fields beyond only catalysis due to this autocatalytic behavior.

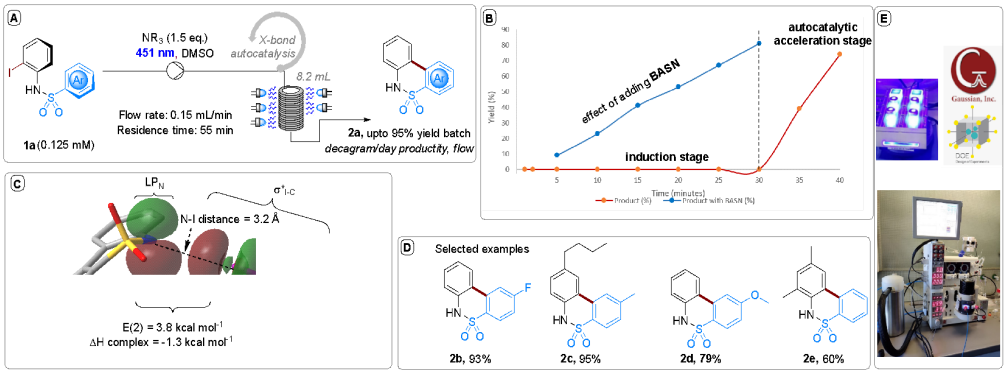

Figure 1: [A] Synthesis of BASN using visible-light autocatalysis in flow set-up, [B] kinetic profile as key proof of autocatalysis, [C] DFT investigation of BASN$^-$-1a halogen bond, [D] selected substrate scope, and [E] reaction set-up in batch (top right) and flow (bottom) along with software (top and middle left) used in the study.

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Photocatalytic oxygen transfer as an innovative route for N_2O upgrading

O. Delaunay, A. Denicourt-Nowicki*, A. Roucoux*

Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR 6226, F-35000 Rennes, France.

**audrey.denicourt@ensc-rennes.fr ; alain.roucoux@ensc-rennes.fr*

Keywords: photocatalysis, nitrous oxide, oxygen transfer, sustainable chemistry, silver on titanium dioxide

Introduction. Nitrous oxide (N_2O) is the third greenhouse gas after carbon dioxide and methane, with a global warming potential of almost 300 times higher compared to CO_2 owing to its long lifetime (114 years) in the atmosphere.[1] The emissions principally arise from chemical industries, for instance those producing nitric or adipic acid, which will have to face more drastic European standards concerning this gas, currently burnt in flares,[2] a destructive and energy-consuming process. In a sustainable way, upgrading N_2O as an oxygen source in oxidation reactions appears relevant, but its activation remains challenging due to its weak reactivity. To alleviate the drastic temperatures generally required, photocatalysis constitutes a milder alternative to activate N_2O and selectively oxidize organic compounds. Herein, we demonstrate the efficient photoactivation of N_2O with silver-doped titanium dioxide and unlock its potential as oxygen atom transfer, using phosphines as molecular probes.[3]

Experimental/methodology. Silver-doped titanium dioxide (Ag/TiO_2) catalyst was easily prepared by a straightforward photodeposition process. Oxidation of phosphines was performed under UV-light irradiation, at nitrous oxide atmosphere (1 bar), with low metal loadings. Composition of the gas phase in the reactor, monitored by GC-BID, was a proof of concept of the efficient decomposition of N_2O into dinitrogen (N_2).

Results and discussion. Silver-doped TiO_2 catalyst specifically activates nitrous oxide at a very low metal loading (0.16 wt%) and the efficient oxygen transfer from N_2O to phosphines under photocatalytic activation in a gas-liquid-solid system was achieved with complete conversion and selectivity, only releasing N_2 as sole benign co-product (Figure 1). Moreover, nitrous oxide is more selective than dioxygen, allowing only transfer to the phosphorus atom without mineralization. The reaction was extended to other phosphines in various organic solvents and also innovatively in water. Finally, the presence of silver was found crucial to catalytically activate N_2O and a mechanism corroborated by blanks experiments was proposed.

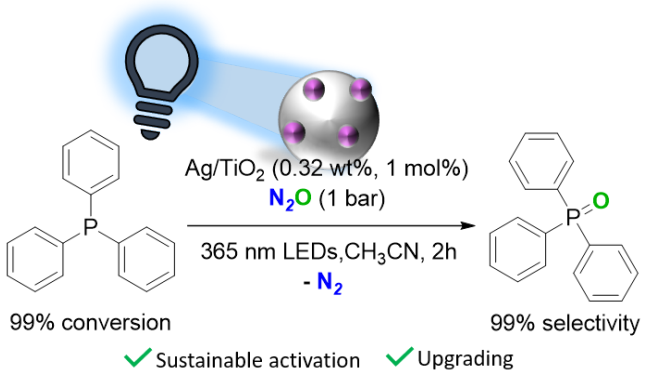

Figure 1. Ag/TiO_2 catalyzed photocatalytic activation of N_2O coupled with oxidation of triphenylphosphine.

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Photocatalysis for artificial photosynthesis aiming at carbon neutral

A. Kudo

Faculty of Science & Carbon Value Research Center, Tokyo University of Science, Tokyo, Japan

Keywords: Photocatalyst, Water splitting, CO_2 reduction, Artificial Photosynthesis, Carbon neutral

Introduction.

Photocatalytic water splitting and CO_2 reduction are promising reactions to solve resources, energy, and environment issues, and achievement of carbon neutral. These reactions are regarded as artificial photosynthesis, because light energy is converted to storable chemical energy. In the present paper, various metal oxide and sulfide photocatalysts and semiconductor photoelectrodes for water splitting and CO_2 reduction using water as an electron donor are introduced and discussed.

Results and discussion.

(1) Photocatalytic water splitting for green H_2 production

$Rh_{0.5}Cr_{1.5}O_3/AgTaO_3$ (BG 3.4 eV) of a valence-band-controlled metal oxide photocatalyst gave 40% of an apparent quantum yield at 340 nm and 0.13% of a solar to hydrogen conversion efficiency [1]. However, this photocatalyst responds to only UV light because of the wide band gap. It is a challenging topic to develop photocatalysts responding to light with long wavelength. Rh and Sb-codoped $SrTiO_3$ photocatalyst loaded with IrO_2 was active for water splitting into H_2 and O_2 under visible light and simulated sunlight irradiations as a single particle type photocatalyst [2]. This photocatalyst responds to 520 nmof visible light. Moreover, we recently developed Ir-doped $SrTiO_3$ that showed the activity for water splitting up to 600 nm of visible light. On the other hand, $SrTiO_3$:Rh and several metal sulfides of a H_2-evolving photocatalyst and $BiVO_4$ of an O_2-evolving photocatalyst constructed various type of Z-schematic photocatalyst systems with Fe^{3+}/Fe^{2+}, $[Co(bpy)_3]^{3+/2+}$, $[Co(phen)_3]^{3+/2+}$, and a conductive reduced graphene oxide (RGO) as an electron mediator and even without an electron mediator [3]. Various types of Z-scheme systems for water splitting under visible light irradiation were also successfully developed by employing Rh- and Ir-doped metal oxide powdered materials with relatively narrow energy gaps (EG) to utilize wide range of visible light [4].

(2) Photocatalytic CO_2 reduction using water as an electron donor for CCU

Ag cocatalyst-loaded $ALa_4Ti_4O_{15}$ (A = Ca, Sr, and Ba) [5] and tantalates photocatalysts [6,7] such as $NaTaO_3$:Ba with 3.79–4.1 eV of band gaps showed activities for CO_2 reduction to form CO and HCOOH in an aqueous medium without any sacrificial reagents. CO is the main reduction product rather than H_2 even in an aqueous medium. Especially, the $Ag/NaTaO_3$:Ba photocatalyst gave ca. 90% of the selectivity for the CO_2 reduction [6]. When Rh-Ru cocatalyst is used instead of Ag, CH_4 was formed with ca. 10% of the selectivity [7]. Thus, an uphill reaction of CO_2 reduction accompanied with water oxidation was achieved using the Ag- and Rh-Ru-loaded metal oxide photocatalysts with wide bandgaps. We also constructed a Z-scheme system consisting of $(CuGa)_{0.5}ZnS_2$ of a CO_2-reducing photocatalyst with $BiVO_4$ of an O_2-evolving photocatalyst and RGO of an electron mediator for CO_2 reduction using water as an electron donor. The Z-scheme system gave H_2, O_2, and CO simultaneously under visible light irradiation [8].

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Photocatalytic production of hydrogen peroxide in seawater

T. Freese[a], J. T. Meijer[a], G. Alachouzos[a], M.C.A. Stuart[a], R. Tarozo[a], D. Gerlach[a], P. Rudolf[a], B. L. Feringa*

a Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. E-mail: b.l.feringa@rug.nl

Keywords: hydrogen peroxide, photocatalysis, heterogeneous catalysis, hydrogen energy, green chemistry

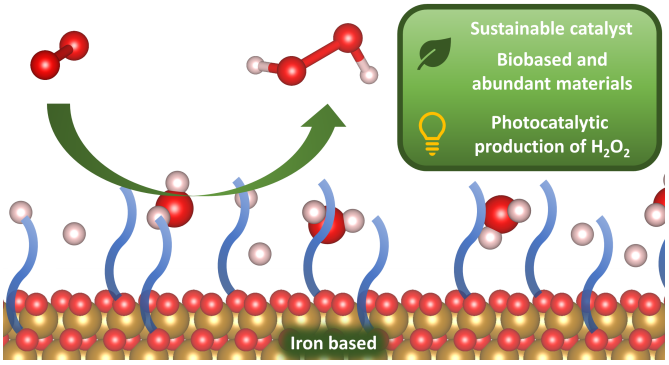

Figure 1: Graphical abstract depicting photocatalytic oxygen reduction to hydrogen peroxide.

Over the last decade, researchers across the globe strived for a more sustainable production of hydrogen peroxide (H_2O_2) as powerful disinfectant, detergent, or oxidant in chemical synthesis.[1] As the global market for H_2O_2 is estimated to grow at a compound annual growth rate (CAGR) of 3.2% to 5.7 million tons by 2027, the demand for a greener alternative to the 80-year-old anthraquinone (AQ) process increases dramatically.[2] Facing climate change, the AQ oxidation process is considered untenable as it produces harmful organic waste and requires significant energy input generated from fossil fuels. As hydrogen peroxide is an efficient and environmentally benign oxidant (H_2O and O_2 as only sideproducts), sustainable modernization of its manufacturing process is key. H_2O_2 recently was suggested as an advantageous energy carrier over H_2 – being fully soluble in water, thus storable, safer operation, and transportation can be realized. A H_2O_2 fuel cell with + 1.09 V vs. the normal hydrogen electrode (NHE) is comparable to a conventional hydrogen fuel cell (+ 1.23 V vs. NHE), consequently utilizing green and sustainable energy sources such as solar energy to produce H_2O_2 directly from water would be a significant breakthrough.[3] The future energy transition towards renewables (solar and wind energy) could lead to the application of H_2O_2 as energy carrier to overcome seasonal and day and night cycles. Thus, the decentralized photocatalytic production of H_2O_2 from O_2 or H_2O on smaller scales could deliver cost-effective dilute H_2O_2 on demand, which is more suitable for a wide range of applications. In this research we are focusing on the development of a new photocatalytic system for the production of H_2O_2 from water and sunlight. Hence skipping the (solar-)electricity needed for water oxidation in electrolyzers and directly utilizing the solar energy to produce H_2O_2 as future energy carrier for the energy transition would be considered as substantial advancement. A new heterogeneous photocatalyst for the formation of H_2O_2 has been developed, based on green principles: Only allowing earth-abundant materials and metals, biomass-based sources for organic compounds as catalyst material, synthesis of the catalyst only in ethanol and avoiding solvent-intense purification techniques (extraction, chromatography etc.). The heterogeneous catalyst material offers for recycling for up to 7 rounds and is producing H_2O_2 with blue light (445 nm) within 5h photocatalytically at room temperature. It was also successfully applied by testing the production of H_2O_2 with real sunlight and in seawater.

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Limitation of molecular twisting: Upgrading a donor-acceptor dye to drive H_2 evolution

Kaijian Zhu,[1] Ainoa Paradelo Rodríguez,[1] Marie Brands,[2] Titus de Haas,[3] Francesco Buda,[3] Joost N.H. Reek,[2] Guido Mul,[1] Annemarie Huijser [1]

[1]*PhotoCatalytic Synthesis Group, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, the Netherlands.*

[2]*Van 't Hoff Institute for Molecular Sciences, Universiteit van Amsterdam, Science Park 904, 1098 XH Amsterdam, the Netherlands.*

[3] *Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, the Netherlands.*

[*]*j.m.huijser@utwente.nl*

Keywords: Photocathode; donor-acceptor dye, molecular twisting, H_2 evolution

The performance of dye-sensitized photoelectrochemical (DSPEC) cells is currently limited by the low efficiency of the photocathode.[1-3] Donor-acceptor (D-A) dyes for photosensitization of the p-type semiconductor have been designed to prolong light-induced charge separation by spatially separating electrons and holes.[4] However, other effects of photoinduced changes on the performance have not been extensively investigated. We demonstrate that photoinduced twisting of a D-A P1 dye adsorbed onto NiO determines the ultrafast dynamics and photoelectrochemical performance. Twisting can be manipulated by co-adsorption of myristic acid, which has a carboxyl anchoring group and a long apolar alkyl chain. Time-resolved photoluminescence and Density Functional Theory studies show that the probability of twisting is lowered by the presence of myristic acid and that this increases the energy levels of the photoexcited state of the D-A dye. The presence of myristic acid also favors light-induced charge separation, as apparent from femtosecond transient absorption, and increases the photocurrent. Very interestingly, only in the presence of myristic acid light-induced H_2 evolution is observed in aqueous media, despite the absence of a H_2 evolution catalyst.(Figure 1b) We assign the H_2 generation to a synergetic effect of inhibited twisting of the D-A dye radical anion increasing its electrochemical potential, combined with adsorption of H^+ on the hydroxylated NiO surface. Our work demonstrates that control of twisting offers a simple design approach for efficient solar fuel devices.

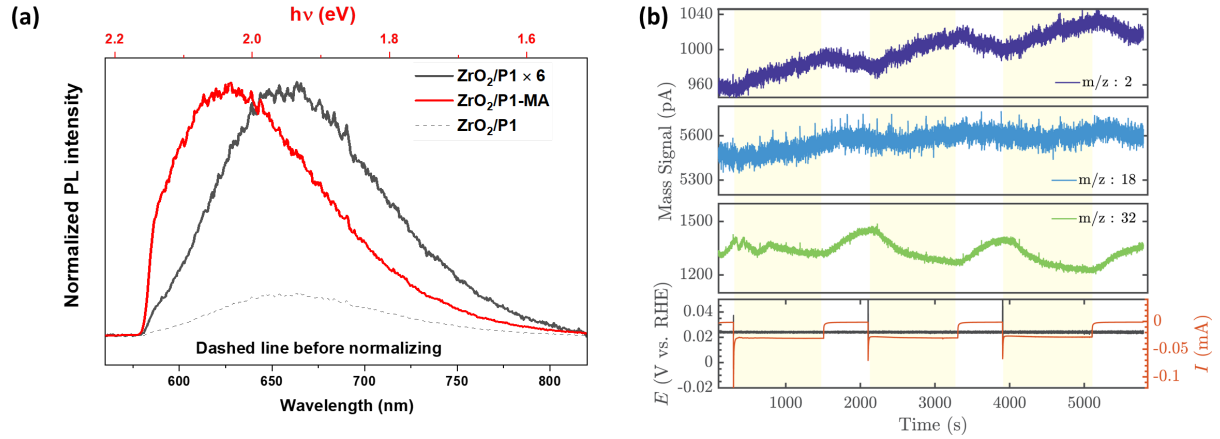

Figure 1. (a)Steady-state photoluminescence spectra of ZrO_2/P1 and ZrO_2/P1-MA recorded by 532 nm excitation in air, detected using a 580 nm long-pass filter to remove residual excitation light. (b) Electrochemical Mass Spectrometry results of NiO/P1-MA at -0.35 V vs. Ag/AgCl with 460 nm LED illumination.

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An efficient metal-organic framework-derived nickel catalyst for the light-driven methanation of CO_2

Angel Sousa[1], Diego Mateo[1], I. Khan, G. Shterk[1], T. Shoinkhorova[1], D. Poloneeva[1], Luis Garzon-Tovar[1], Jorge Gascon[1*]

[1]*King Abdullah University of Science and Technology (KAUST), KAUST Catalysis Center (KCC), Advanced Catalytic Materials, Thuwal, 23955, Kingdom of Saudi Arabia*
[*]*jorge.gascon@kaust.edu.sa*

Introduction

Photo-thermal catalysis offers the advantage of exploiting both thermal and non-thermal contributions of sunlight[1], overcoming the inherent limitations of traditional photochemical processes. This approach offers the possibility to produce the so-called solar fuels from carbon dioxide (CO_2) and thus represents a promising approach not only to alleviate CO_2 emissions but also to efficiently store renewable energy in the form of chemical bonds. In this work, we demonstrate the synthesis of Ni NPs dispersed on a carbon matrix via controlled pyrolysis at different temperatures of a metal-organic framework (MOF) precursor. The optimized catalyst was tested in the light-mediated CO_2 methanation reaction, displaying high conversion rates, selectivity, and long-term stability.

Experimental/methodology

Ni-MOF-74 was synthesized according to the reported method[3]. Once synthesized, Ni-MOF-74 was pyrolyzed in a tubular oven under a continuous flow of N_2 for 6 hours at temperatures of 500, 600, and 700 ºC. Samples were characterized by powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The catalytic activity was tested in a batch quartz reactor using a 300 W Xe lamp as light source.

Results and discussion

Among all the samples, Ni@C-600 displayed the highest temperature under light radiation, thus leading to very high CH_4 production rates of 488 mmol g^{-1} h^{-1} (Figure 1a). Further mechanistic studies revealed that the system is mainly operated by a light-to-heat conversion. We also performed an additional catalytic test using a flow-type reactor and, under optimal conditions, the Ni@C-600 catalyst exhibited a notable CO_2 conversion ranging from 42 to 57 % after more than 12 consecutive hours of reaction without evident deactivation (Figure 1b)[4].

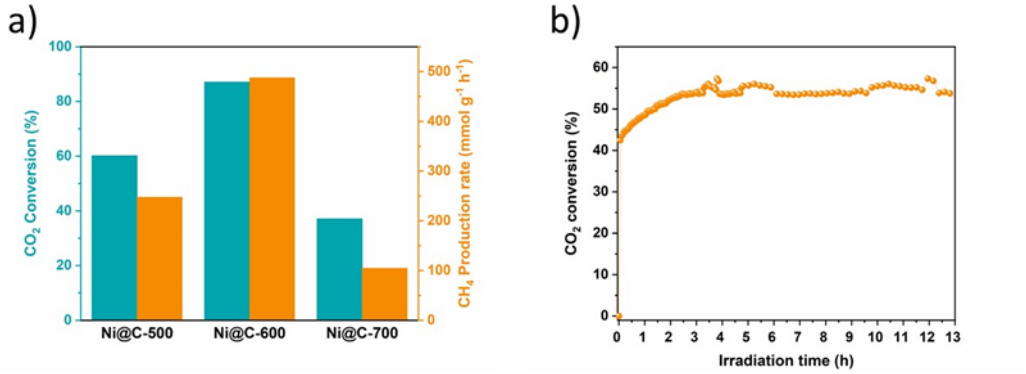

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Photo-electrochemical Oxygen Evolution Activity in Nickel and Cobalt Antimonates

Michal Bajdich[1], Karun K. Rao,[1,2] Lan Zhou,[3,4] Pooja Basera, Yungchieh Lai,[3,4] Matthias H. Richter,[3,4] Xiang Li,[5,6] Yubing Lu,[7] Junko Yano,[6,7] John M. Gregoire[3,4,*]

[1] *SUNCAT Center for Interface Science and Catalysis and Liquid Sunlight Alliance, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*
[2] *Department of Chemical Engineering, Stanford University, Stanford, CA, USA*
[3] *Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA, USA*
[4] *Liquid Sunlight Alliance, California Institute of Technology, Pasadena, CA 91125, USA*
[5] *SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA*
[6] *Liquid Sunlight Alliance, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*
[7] *Molecular Biophysics and Integrated Bioimaging Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

Keywords: photocatalysis, water splitting, liquid solar fuels, Density functional theory

Introduction. Renewable generation of fuels via solar energy offers promising pathways towards sustainable energy future. Its deployment hinges on the discovery of electrochemically durable materials with good solar-to-chemical conversion efficiency. Prerequisite visible spectrum photoresponse from electrochemically stable materials is however quite rare. On the other hand, the oxygen evolution reaction (OER) requires electrodes that are not only catalytically active, but also stable under harsh electrochemical environments

Methodology. Electronic Structure Calculations of bulk geometries and surface slabs were perfromed at the spin-polarized, GGA Hubbard U-level within the computational hydrogen electrode model. Composition library synthesis and XRD/TEM/XAS characterization and OER Catalytic and Photo-electrochemistry measurements

Results and discussion. In this talk, we report on and theoretical understanding of photo-electrochemical behavior an amorphous and crystaline versions of Ni-Sb-Ox and Co-Sb-Ox oxide photoanodes discovered via high-throughput experimental screening. The newly discovered amorphous phases [1, 2] meet the requirements of operational stability, visible photoresponse, and appreciable photovoltage. Guided by experimental X-ray absorption characterization of these systems we use density functional theory calculations to perform a prototype phase search to identify a broad family of stable and metastable mixed rutile and hexagonal-like phases for other compositions [3]. Detailed Pourbaix analysis of the identified phases show excellent electrochemical stability, consistent with experimentally measured low metal ion concentrations in the electrolyte of photoelectrochemical cells. We analyze when he identified phases form favorable oxygen vacancies formation energies under the reducing synthesis conditions which match measured Ni K-edge x-ray absorption spectra. The calculated OER overpotentials for the most active sites decreases with increasing Ni/Co content, which captures the experimentally observed trend. Stable amorphous metal-antimonates photoanodes established are important systems for computational understanding of both the structural and catalytic behavior of these complex oxides and elucidating the co-optimization of activity and durability in metal antimonates.

Acknowledgments
This material is based on work performed by the Liquid Sunlight Alliance, which is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Fuels from Sunlight Hub under award DE-SC0021266.

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Modulating the Nanostructure of Carbon Nitride for Improved Continuous-Flow Trifluoromethylation of (Hetero)Arenes

Alessandra Sivo[1], Vincenzo Ruta[1], Dr. Mark A. Bajada[1], Prof. Dr. Gianvito Vilé[1]*

[1]*Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano (Italy)*
[*]*Corresponding author email: gianvito.vile@polimi.it*

Introduction. In recent years, visible light catalysis has emerged as a game-changing technology for creating a new generation of chemical processes. However, scaling up these reactions has proven difficult due to light transmission limitations in batch reactors and the high cost of commonly-employed Ir or Ru-based homogeneous photocatalysts [1]. For example, trifluoromethylation reactions, widely used in fine chemical production, rely heavily on batch methods and expensive transition metals. Herein, we report using metal-free carbon nitride, a material with excellent photostability and adjustable surface area [2], for the trifluoromethylation of heteroarenes, examining the impact of catalyst structuring to enhance reaction efficiency and production capacity. This approach offers new possibilities for scalable, cost-effective trifluoromethylation of heteroarenes.

Experimental/methodology. The catalysts in powdered and structured form were characterized via various techniques, such as XRD, N_2 physisorption, XPS; XAS, TEM, FIB-SEM, and tomography. A structured reactor was contructed using a FEP tube (2 mm internal diameter, 500 mm length) fileld with a mixture of base (1.32 mmol), glass beads (2.4 g), and catalyst (50 mg). The (hetero)aryl reagent and TfCl were introduced via syringe pumps into the assembled photoreactor. The reaction mixture was exposed to light using a PhotoCube reactor. Yields and conversions were determined by ^{1}H, ^{13}C NMR, and HPLC.

Results and discussion. Initial batch photocatalytic studies showed that mesoporous graphitic carbon nitride ($mpgC_3N_4$) had superior catalytic properties compared to bulk graphitic (gC_3N_4) and nanosheet (nC_3N_4) carbon nitrides, resulting in a substantial increase in yield of trifluoromethylpyrrole (from 6 to 80%), at 60 min. Flow technology was adopted in order to provide a uniform radiation distribution inside the reactor, and satisfy the constraints imposed by the Beer-Lambert Law for photoinduced chemical transformations. We demonstrated that the packed-bed and structured reactor designs with porous framework of $mpgC_3N_4$ offered a unique environment to scale-up the process and minimize mass transfer limitations of the multicomponent reaction, showing an increase in the production rate of the desired model trifluoromethylpyrrole of almost 50%, in relation to the batch method. Also, the use of glass beads and polymeric structural motifs as a packing material reduced particle competition for the absorption of visible-light photons. The stability of the catalyst (as verified by time-on-stream analysis) and the facile recyclability of the photocatalytic system (as a consequence of the immobilization of $mpgC_3N_4$) corroborated the importance of continuous flow reactor design for the photocatalyzed trifluoromethylation process. The protocol was successfully applied to trifluoromethylate pyrroles, indoles, and imidazoles, demonstrating the technique's versatility for various compounds.

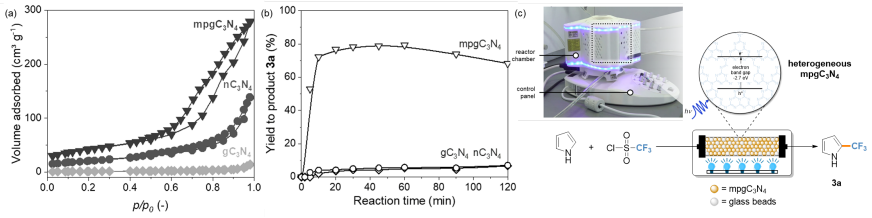

Figure 1. N_2 physisorptions of nC_3N_4, nC_3N_4, and $mpgC_3N_4$ catalysts (a), comparison of the microkinetic performance of the catalysts at T = 40°C (b), sketch of the structured photoreactor (d).

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Modulating the Nanostructure of Carbon Nitride for Improved Continuous-Flow Trifluoromethylation of (Hetero)Arenes

Alessandra Sivo[1], Vincenzo Ruta[1], Dr. Mark A. Bajada[1], Prof. Dr. Gianvito Vilé[1]*

[1]*Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano (Italy)*
[*]*Corresponding author email: gianvito.vile@polimi.it*

Introduction. In recent years, visible light catalysis has emerged as a game-changing technology for creating a new generation of chemical processes. However, scaling up these reactions has proven difficult due to light transmission limitations in batch reactors and the high cost of commonly-employed Ir or Ru-based homogeneous photocatalysts [1]. For example, trifluoromethylation reactions, widely used in fine chemical production, rely heavily on batch methods and expensive transition metals. Herein, we report using metal-free carbon nitride, a material with excellent photostability and adjustable surface area [2], for the trifluoromethylation of heteroarenes, examining the impact of catalyst structuring to enhance reaction efficiency and production capacity. This approach offers new possibilities for scalable, cost-effective trifluoromethylation of heteroarenes.

Experimental/methodology. The catalysts in powdered and structured form were characterized via various techniques, such as XRD, N_2 physisorption, XPS; XAS, TEM, FIB-SEM, and tomography. A structured reactor was contructed using a FEP tube (2 mm internal diameter, 500 mm length) fileld with a mixture of base (1.32 mmol), glass beads (2.4 g), and catalyst (50 mg). The (hetero)aryl reagent and TfCl were introduced via syringe pumps into the assembled photoreactor. The reaction mixture was exposed to light using a PhotoCube reactor. Yields and conversions were determined by ^{1}H, ^{13}C NMR, and HPLC.

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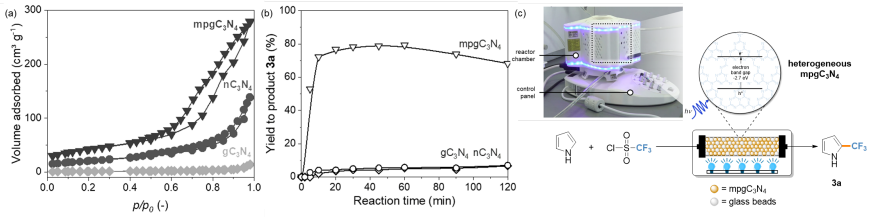

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Surface molecularization of plasmonic systems for photo-redox catalysis

R. Bericat-Vadell[1*], P.Senkar[1], X. Zou[1], J. Sá[1, 2]

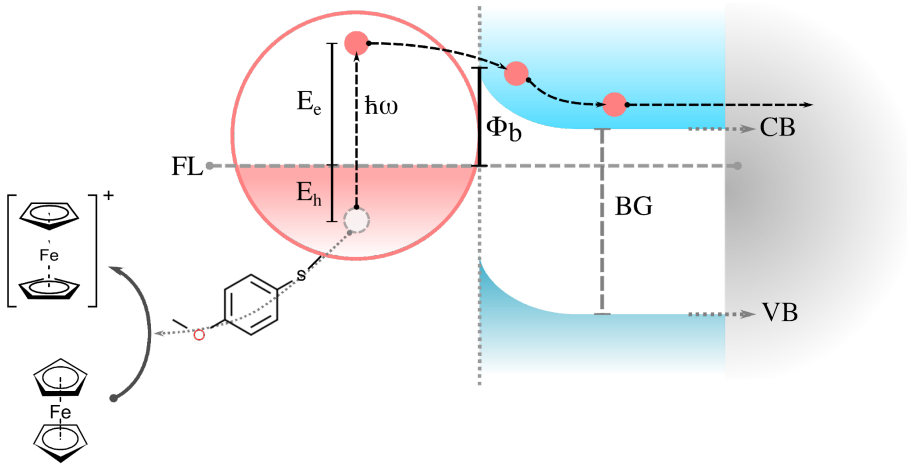
[1]*Physical Chemistry Division, Department of Chemistry – Ångström, Uppsala University, Uppsala, Sweden.*
[2]*Institute of Physical Cemistry, Polish Academy of Sciences, Warsaw, Poland.*
[*]*robert.bericat.vadell@kemi.uu.se*

Keywords: Plasmonics, Photo-redox catalysis, Ultrafast Time-Resolved Spectroscopy, Chronoamperometry.

Introduction. Organic photo-redox catalysis is one of the fastest growing fields in the research on Organic Chemistry, with high relevance for both the academic and industrial sector. Currently, the most frequently used light absorbers, also termed photocatalysts, are transition metal complexes or organic pigments that have been known for many decades. We argue that some approaches fundamentally different from these traditional means to initiate the photochemical reactions have the potential to open up new avenues in the field. In this sense, our research is focused on the development of novel gold plasmonic nano-hybrid architecture as light absorbers, aimed at photo-redox organic synthesis. More specifically, the project presented herein studies "molecularization" strategies for plasmonic systems; we design catalytic systems where plasmonic structures can behave as molecular catalysts. The aim with this research is to merge the qualities of plasmonic systems (efficient and tuneable absorption of light) with those of molecular photo-systems (single charge transfer capabilities and high chemical selectivity).

Experimental/methodology. To fabricate the studied systems, the surface of our plasmonic structure is functionalized with molecules (thiols) capable of acting as catalytic centres. During photoexcitation, hot carriers are generated at the plasmonic nanoparticle. Hot electrons inject in the n-type semiconductor (TiO2) and subsequently travel to the electrode, while hot holes are transferred first to the thiols and from there are used to oxidise ferrocene. The photo-system photocatalytic performance is tested via ultrafast transient spectroscopy and electrochemical studies, which provide information on the system capability of converting light into charge carriers and then oxidising the substrate.

Results and discussion. For the time being, we have already gathered spectral evidence of the charge transfer between the plasmonic gold (light absorber), the attached thiol (4-methoxythiophenol) and TiO2. We have also measured photocurrents associated to the oxidation of ferrrocene by our photocatalytic system.



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Hydrogenation of styrene via plasmon-induced photodissociation of hydrogen molecule over Au/ZrO_2

T. Okamoto[1], E. Fudo[1], A. Tanaka[2], H. Kominami[2*]

[1]*Molecular and Material Engineering, Kindai University, Higashiosaka, Japan*
[2]*Department of Applied Chemistry, Kindai University, Higashiosaka, Japan*
[*]*hiro@apch.kindai.ac.jp*

Keywords: gold nanoparticle, surface plasmon resonance, photodissociation

Introduction. Gold(Au) nanoparticles possess unique properties and absorb visible light at around 550 nm due to a phenomenon called surface plasmon resonance (SPR). Two main mechanisms have been proposed for reactions over plasmonic photocatalysts. One of them is a plasmon-induced electron transfer mechanism; hot electrons are injected to the conduction band of metal oxides and then redox reactions proceed. Various plasmon-induced reactions such as water splitting and hydrogen production have been reported [1][2]. The other is a direct molecule activation mechanism; transfer of electrons from Au particles to molecules in a specific electronic state induces dissociation and desorption of the molecules. In previous study, it was reported that hydrogen (H_2) molecules are dissociatively adsorbed on Au nanoparticles under irradiation of visible light[3]. However, this dissociated hydrogen has not been used for hydrogenation reaction. Therefore, we attempted to use hydrogen photodissociatively adsorbed on Au particles for hydrogenation of organic compounds. In this study, we investigated hydrogenation of styrene (ST) to ethylbenzene (EB) over Au/ZrO_2 and propose the expected mechanism of this reaction.

Experimental/methodology. Au/ZrO_2 was prepared by a deposition-precipitation method. The ZrO_2 powder was suspended in 100 cm^3 of an aqueous solution containing an $HAuCl_4$ and NaOH. The suspension was stirred at 343 K for 2 h and the resultant powder was thermally treated in a tubular furnace under a flow of H_2 at 527 K for 2 h. Au/ZrO_2 (50 mg) was suspended in 5 cm^3 of an acetnitrile solution in a test tube and, after replacing the gas phase with H_2, ST (*ca*. 30 μmol) was added. The test tube was photoirradiated at 20°C with a green LED. The liquid phase after the reaction was analyzed with a gas chromatograph.

Results and discussion. Hydrogenation of ST over Au/ZrO_2 did not occur under the dark, indicating that hydrogen molecules are not dissociatively adsorbed on Au particles in the dark. On the othe hand, under irradiation of visible light, ST was hydrogenated to EB, which means that H_2 molecules are dissociated on Au particles under light irradiation and can be used for the hydrogenation. To determine whether the observed reaction occurs via a plasmon-induced process, we collected the action spectrum. Figure shows the absorption spectrum of Au/ZrO_2 and the action spectrum of hydrogenation of ST over Au/ZrO_2. Apparent quantum efficiency (AQE) at each centered wavelength of light was calculated from the ratio of the double amount of EB and the amount of photons irradiated using the following equation.

$$\mathrm{AQE}=\frac{2\times \text{the amount of EB}}{\text{the amount of incident photon}}\times 100$$

As shown in Figure, the tendency of AQE was similar to the absorption spectrum of Au/ZrO_2. Therefore, it can be concluded that hydrogenation of ST to EB over Au/ZrO_2 was induced by photoabsorption due to SPR of Au nanoparticles.

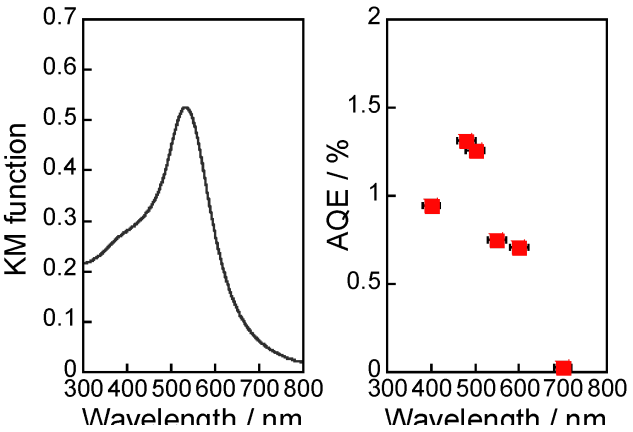

Figure Absorption spectrum of Au/ZrO_2 (left) and action spectrum of Au/ZrO_2 in hydrogenation of ST to EB (right).

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Photocatalyzed Trifluoromethylthiolation of Activated Alkenes with CF_3SO_2Na

Fangming Chen[1], Wenbin Yi[1 *]

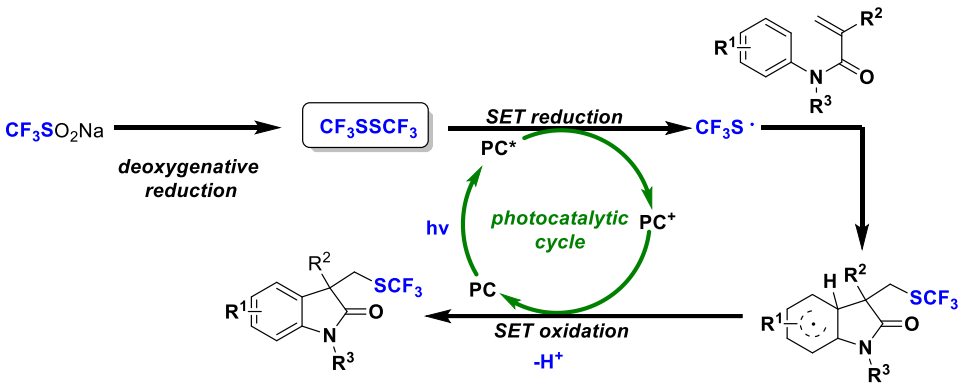
[1]*Nanjing University of Science and Technology, Nanjing, P.R. China*
[*]*Corresponding Author's E-mail : yiwb@njust.edu.cn*

Keywords: Trifluoromethylthiolation, Photocatalysis, Radical, Difunctionalization, Alkenes.

Introduction. Trifluoromethylthio (SCF_3) group is considered to have excellent lipophilicity due to its high Hansch's hydrophobicity parameter (π = 1.44).Thus it is highly desirable to develop practical synthetic methods for the introduction of SCF_3 group. Langlois reagent (CF_3SO_2Na) [1], which has cheap price and stable properties, is a well-known radical trifluoro-methylation reagent.[2] Recently,we developed a novel and practical trifluoromethylthiolation of activated alkenes with CF_3SO_2Na through deoxygenative reduction and photoredox radical processes, which present an unprece-dented application of CF_3SO_2Na as a radical SCF_3 source.

Experimental/methodology. A 25 mL Schlenk flask equipped with a magnetic stir bar was charged with $Ir(ppy)_3$ (1.7 mg, 0.001 mmol, 0.5 mol%) .The flask was evacuated and refilled with N_2 for three times. The vessel was then charged with dry MeCN (4.0 mL), activated alkene (0.5 mmol, 1.0 equiv), PPh_3 (655mg, 2.5 mmol, 5 equiv) and CF_3SO_2Na (234mg, 1.5 mmol, 3.0 equiv) .The flask was placed at a distance of 2 cm from the blue LED. The mixture was stirred under nitrogen atmosphere and irradiated by blue LED for 6 h. Upon completion, the volatiles were removed under vacuum and the residue was purified by column chromatography to give the corresponding products.

Results and discussion. We investigated the scope of the transformation with respect to the aldehydes. A variety of N-methyl-N-phenylmethacryl amides with substituents at para, meta, as well as ortho positions (R^1) in the aniline ring were aryltrifluoromethylthiolated smoothly to give the corresponding oxindoles in moderate to good yields (75-83% yield). The substitute effect at the α-position (R^2) of the acrylamides was next explored, and it was found that several α-sustitutents, including benzyl, methoxyl, and ester, were compatible with this transformation to furnish the desired products in good yields (75-83% yield). Substrates with different protecting groups (R^3) also performed well (70-73% yield).



Acknowledgments
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CO_2 Hydrogenation with Plasmonic Nanomaterials: Black Gold and Nickel Nitride Nanosheets

Rishi Verma, Saideep Singh, and Vivek Polshettiwar*

Department of Chemical Sciences, Tata Institute of Fundamental Research (TIFR), Mumbai, India

Email id: rishi.verma@tifr.res.in, vivekpol@tifr.res.in

Abstract

Localized surface plasmon resonance (LSPR) enables solar light catalysis of difficult reactions by generating hot charge carriers on the nanoparticle surface, leading to novel and targeted reaction pathways.[1-5] For efficient light absorption and catalytic activity, the photocatalyst should absorb the whole solar broadband spectrum. Dendritic plasmonic colloidosomes (DPC-C4)[6], commonly known as "black gold," a recently discovered novel nanomaterial from our group, might be a good option. Black gold, comprising Au nanoparticles on nanosilica (DFNS)[7], displays high absorbance of visible and near-infrared light due to its heterogeneous particle size distribution and interparticle lengths. However, its hot electron transfer efficiency is limited.[6] To extract these hot electrons, we then synthesized black gold loaded with nickel sites (DPC-C4-Ni).[8] Under light excitation, DPC-C4-Ni excel over DPC-C4 and DFNS-Ni in terms of photocatalytic CO_2 hydrogenation activities. DPC-C4-Ni shows a very high photocatalytic CO production rate (2464 ± 40 mmol g_{Ni}^{-1} h^{-1}) with 95 % CO selectivity. Notably, the reaction was carried out in a flow reactor at low temperature and atmospheric pressure without external heating. The photocatalyst was stable for at least 100 h.[8]

Although black gold-nickel displayed promising catalytic activity for CO_2 hydrogenation, the requirement for high light intensity is a critical aspect to address. As an alternative, we suggest exploring the potential of hydroxy-terminated nickel nitride (Ni_3N) nanosheets as a feasible substitute for traditional plasmonic metals.[9] The synthesized Ni_3N nanosheets exhibited broadband light absorption spanning from visible to near-infrared regions of the solar spectrum. The Ni_3N nanosheets showed an excellent CO production rate (ca. 1212 mmol g^{-1} h^{-1}) and 99 % selectivity towards CO under flow conditions using visible light (although it also required high light power).[9]

The photocatalytic CO_2 hydrogenation reaction mechanism and the role of non-thermal versus the thermal effect of plasmonic catalysis in the case of DPC-C4-Ni and Ni_3N nanosheets were further explored by using (i) finite-difference time-domain simulations (FDTD), (ii) light-intensity-dependent production rate, (iii) light-intensity-dependent photocatalytic quantum efficiencies, (iv) wavelength-dependent production rate, (v) kinetic isotope effect (KIE), (vi) temperature program stability study of Ni_3N nanosheets, (vii) *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and (viii) ultrafast transient absorption spectroscopy studies.[8,9]

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The influence of exposed facets of TiO_2 crystals on photocatalytic reduction of nitroaromatic compounds

W. Adamowicz[1,2*], M. Kobielusz[1*], W. Macyk[1*]

[1]*Faculty of Chemistry, Jagiellonian University, ul. Gronostajowa 2, 30-387 Kraków, Poland*
[2] *Doctoral School of Exact and Natural Sciences, Jagiellonian University, ul. Łojasiewicza 11, 30-348 Kraków, Poland*
[*]*wiktoria.adamowicz@doctoral.uj.edu.pl, kobielusz@chemia.uj.edu.pl, macyk@chemia.uj.edu.pl*

Keywords: Tailored crystals; Anatase; TiO_2; Nitroaromatics; Photocatalysis

Introduction. Titanium dioxide is one of the most widely used materials in photocatalysis. This material has also been established to be very active in organic synthesis reactions, including the reduction of nitroaromatic compounds. The crystallographic facets of titanium dioxide (especially anatase crystal facets) differ in their photocatalytic properties [1]. Upon UV light irradiation, the photogenerated charges, electrons and holes, segregate into the facets of tailored crystals. As a result, the particular facets become enriched with holes or electrons. In general, depending on the proceeding photocatalytic reaction (reduction or oxidation), crystals with predominantly exposed different facets should be considered as favoured photocatalysts. Furthermore, different atomic arrangements, as well as Ti-O-Ti bond angles at various exposed facets, can differently interact with reagents. The impact of exposed facets in the context of photocatalytic organic synthesis, in particular the reduction of nitroaromatic compounds, has so far been studied to a limited extent.

Experimental/methodology. The phase compositions and crystal shapes of materials were studied by powder X-ray diffraction and scanning electron microscopy. The photocatalytic reduction reactions were conducted with 3-nitrophenol and 1-iodo-4-nitrobenzene. The changes in the concentration of substrate and products were detected with HPLC analysis. The electron transfer activity of TiO_2 electrodes was measured using a rotating disk electrode.

Results and discussion. The studies showed that the photocatalytic reduction of nitroaromatic compounds (3-nitrophenol and 1-iodo-4-nitrobenezene) strongly depends on the exposed facets and increases in the order: sheets, tetragonal truncated bipyramids, belts, showing the predominant role of the {100} facet.

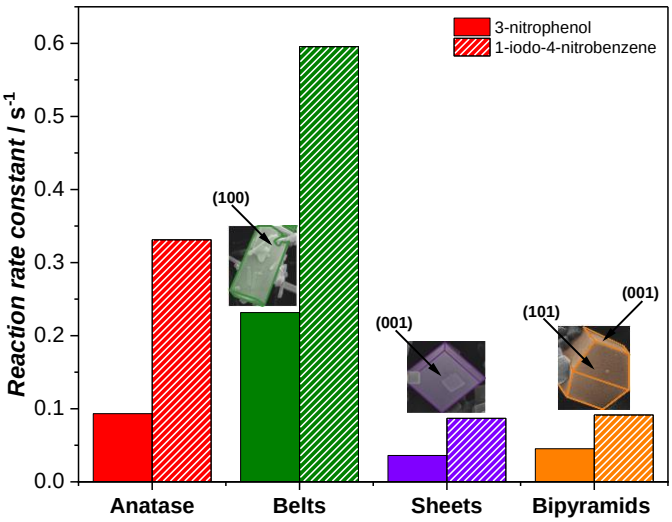

Fig. 1. Reaction rate constants at tailored anatase-TiO_2 in reduction of 3-nitrophenol and 1-iodo-4-nitrobenzene.

Acknowledgements
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H_2 Production by plastics photoreforming using SiC-g-C_3N_4 composites

Maria Teresa Armeli Iapichino [1*], Stefano Andrea Balsamo[1], Roberto Fiorenza [1], Salvatore Scirè[1]

[1]*University of Catania, Department of Chemical Sciences - Catania (Italy)*
*maria.armeliiapichino@phd.unict.it

Keywords: Carbon nitride, silicon carbide, Hydrogen, Photoreforming.

Introduction. Hydrogen is regarded as one of the most promising energy carrier thanks to its high energy density and its lower heating value. One of the green ways to obtain hydrogen is photocatalysis through solar photoreforming of water. This process combines the water reduction with the organic oxidation on a semiconductor material. In a typical process, the electrons in the photocatalyst are excited by sunlight to the conduction band (CB) and these reduce the protons of water to H_2. The choice of the organic substrate is fundamental to drive selectively the byproducts formation with the contextual H_2 evolution, and to enhance the charge carriers separation on the surface of the photocatalysts, being the organic substrate a holes scavenger. In this context, bisphenol A (BPA) and polyethylene terephthalate (PET), employed as sacrificial agents, can play an important role also considering the plastics water pollution. However, one of the necessary steps for the photoreforming reaction is the efficient solubilization of these organic substrates by various pre-treatments, that requires hard conditions which can deactivate the photocatalysts [1]. The focus of this work is the study of uncommon photocatalysts as silicon carbide (SiC) coupled with graphitic carbon nitride (g-C_3N_4). The SiC is a widely used semiconductor in the electronic industries which can be employed as photocatalyst in the plastics photoreforming due to its high mechanical and chemical resistance. The employment of the g-C_3N_4 can improve the activity with the formation of heterojunctions with the main photocatalyst.

Experimental/methodology. To obtain the SiC-g-C_3N_4 composites, the silicon carbide (Sigma Aldrich) was mixed with different amounts of urea and treated at 450°C for 5h with a 5°C/min ramp to favor the thermodegradation of urea and the formation of g-C_3N_4 with different wt%. The sacrificial agents were BPA (Sigma-Aldrich) and PET from commercial bottles. Photocatalytic tests were carried out in a Pyrex reactor irradiated with a solar lamp for 5h. 0,05 g of photocatalyst, 10 ml of a solution of dissolved organic substrates (after the pretreatments) and 40 ml of water were placed inside the reactor at T=30°C. The H_2 was quantified with GC-TCD [2]. The samples were characterized by UV-DRS, XRD, XPS, N_2 adsorption-desorption measurements and TEM.

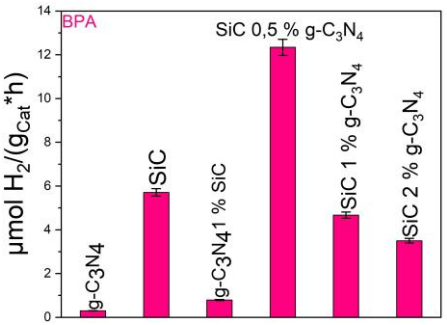

Figure 1 Photocatalytic H_2 production by photoreforming of BPA (pH=13)

Results and discussion. From Fig. 1 it is possible to note as the SiC 0,5% g-C_3N_4 sample was the most active towards the BPA photoreforming providing at an alkaline pH (13) 12 μmol H_2/g_{cat}·h. The same photocatalyst was the most active for the PET photoreforming, obtaining a minor amount of H_2 (2,7 μmol H_2/g_{cat}·h). No H_2 was produced at acid pH for both BPA and PET photoreforming, pointing to the strong influence on the photocatalytic activity of the pretreatment conditions of the organic substrates. Interestingly, a higher amount of g-C_3N_4 was detrimental for the activity, due to the covering of the SiC surface sites by the excess of carbon nitride. A low amount of g-C_3N_4 was essential for the formation of a SiC g-C_3N_4 heterojunction, that favored a strong interaction between the two components, as verified by the characterization measurements. The examined solar photoreforming reactions appear promising for an even more sustainable H_2 economy. The good interaction between unconventional photocatalysts as SiC and g-C_3N_4 allowed to explore new and green ways for the production of H_2 from plastic wastes.

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α-Fe_2O_3–'CuO' nano-heterostructure for efficient photoelectrocatalytic water oxidation using a Cu-complex

T. Benkó[1*], S. Shen[2], M. Németh[1], D. Lukács[1], J. S. Pap[1]

[1]*Centre for Energy Research, Institute for Energy Security and Environmental Safety, Surface Chemistry and Catalysis Department, Budapest, Hungary.*
[2]*International Research Center for Renewable Energy (IRCRE), State Key Laboratory of Multiphase Flow in Power Engineering (MFPE), Xi'an Jiaotong University, Xi'an, China.*
**timea.benko@ek-cer.hu*

Keywords: α-Fe_2O_3 photoanode, CuO, solar water splitting

Hematite (α-Fe_2O_3) can be an ideal photoanode material in photoelectrochemical (PEC) water splitting due to a suitable bandgap, proper band edge positions and low cost. However, the performance of hematite is limited by poor electronic conductivity, high density of surface states, short hole lifetime, and slow kinetics for oxygen evolution at the electrode/electrolyte interface. The design of α-Fe_2O_3 heterostructure is a promising route for improved PEC performance.

Instead of expensive noble metal-based compounds, we introduced a Cu-based water oxidation catalyst on a nanostructured α-Fe_2O_3 semiconductor. In our earlier study [1], the Cu-triglycine pre-catalyst complex resulted in $Cu_2O/CuO/Cu(OH)_2$ nanoparticle coating on indium tin oxide working electrode under the conditions of water oxidation electrocatalysis. This coating acted as an excellent electrocatalyst for water oxidation. Therefore, in this work, the α-Fe_2O_3 photoanode grown on Ti substrate was modified with 'CuO' cocatalyst by the electrodeposition of the Cu-triglycine complex. The resulting hybrid nanostructure, 'CuO'/α-Fe_2O_3, exhibited improved photocurrent density, charge separation and charge transfer efficiency, and lowered charge transfer resistance compared to the α-Fe_2O_3 in PEC water oxidation under full spectrum irradiation.

To achieve high PEC performance, the proper attachment of the cocatalyst on the surface is essential, which depends on the preparation process and the contact between the 'CuO' and the hematite surface. The results on the PEC water oxidation of 'CuO'/α-Fe_2O_3 were compared to photoanodes derived from Cu salts deposited on α-Fe_2O_3 in order to show the beneficial effect of the metal complex used for the synthesis of the active cocatalyst on a semiconductor photoanode [2].

Acknowledgments

This work was funded by the National Research, Innovation and Development Office of Hungary, grant numbers NKFI-128841 and TKP2021-NKTA-05, RRF-2.3.1-21-2022-00009 and the National Key Research and Development Program of China (2018YFB1502003).

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Induced-aggregates in P25 photocatalyst: An unexplored approach to reduce the noble metal co-catalyst content

Enqi Bu[1,*], Xiaowei Chen[1], Carlos López-Cartes[2], Antonio Monzón[3], Juan José Delgado[1,*]

[1]*Departamento de Ciencia de los Materiales, Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cadiz, Campus Río San Pedro, Puerto Real (Cádiz), Spain*
[2]*Departamento de Química Inorgánica. Facultad de Química. Universidad de Sevilla, Sevilla, Spain*
[3]*Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza, Spain*

**Corresponding Author: enqi.bu@uca.es, juanjose.delgado@uca.es*

Keywords: ethanol photoreforming, P25, hydrogen production, in situ photodeposition, aggregates

Introduction. One of the most efficient photocatalysts for the photo-reforming hydrogen production is still based on the use of P25 in combination with Pt, which acts as co-catalyst[1]. However, such high cost of noble metals may hinder the practical application of this emerging technology. Herein, a significant enhancement of ethanol photoreforming hydrogen production over P25 was achieved through a simple process to create TiO_2 aggretates, assisted with in situ photodeposition of a lower content of Pt (0.05 wt%). A mechanism of enhancement and deactivation was then proposed based on the obtained results.

Experimental. The commercial Acros Organics aeroxide P25 was used as the raw photocatalyst. The aggregations were formed by the filtration of different titania suspensions. The reproducibility of this method was evaluated by replicating the synthesis more than 10 time.

Results and discussion. The results of XRD, XPS, N_2 adsorption-desorption and UV-Vis diffuse reflectance analyses indicate that the IA-P25 aggregates were successfully created without modifying the chemical and structural characteristics of the original P25. Based on SEM images, the average aggregate size of IA-P25 was measured to be 35.4 ± 2.1 µm, which is approximately 10 times larger than that of P25. According to the hydrogen production results (Figure 1), the IA-P25 presented significantly higher activities than the raw P25. Additionally, distinct deactivation behaviors could be observed between them, which could be attributed not only to the interaction of Pt atoms and oxygen vacancies, but also to the constant accumulation of intermediates[2]. After ultrasound treatment, IA-P25 showed a very similar activity as raw P25, indicating that the formation of TiO_2 aggregates was the main reason for the improvement and deactivation. Based on all results, the utilization efficiency of TiO_2 particles in IA-P25 with the presence of low content Pt was considered to be higher than in raw P25 benefiting from the formation of aggregates, which facilitated the transfer of photogenerated charge carriers from TiO_2 particles to the surface of Pt for hydrogen evolution, instead of recombination.

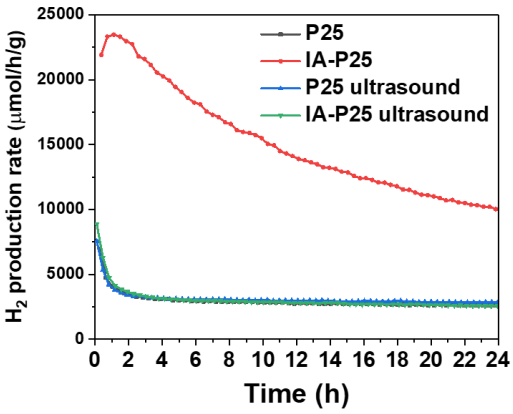

Figure 1. Photocatalytic hydrogen production rate of samples with 0.05 wt% Pt.

Acknowledgments
This work has been supported by the Ministry of Science, Innovation and Universities of Spain with project reference numbers of PID2020-113809RB-C31 and PID2020-113809RB-C33.

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Sunlight-powered reverse water gas shift reaction catalyzed by plasmonic Au/TiO_2: distinguishing between photothermal and non-thermal contributors

P. Buskens[1,2,*], F. Sastre[1], M. Xu[1], N. Meulendijks[1], J. van den Ham[1], J. Rohlfs[1], A. Sanderse[1], R. Habets[1], P. Martínez Molina[1]

[1]*The Netherlands Organisation for Applied Scientific Research (TNO), Eindhoven, The Netherlands*
[2]*Hasselt University, Diepenbeek, Belgium*
[*]*pascal.buskens@tno.nl*

Keywords: plasmon catalysis, photocatalysis, syngas, CCU, *in operando* monitoring

Introduction. To proceed towards an energy and climate neutral chemical industry, it is vital to use sustainable energy and carbon sources for the production of carbon containing chemicals and fuels. Sunlight-powered chemical processes using biogenic CO_2 as feedstock fulfill these requirements. Here, we present the sunlight-powered conversion of CO_2 and green H_2 to CO, catalyzed by TiO_2-supported plasmonic Au nanocatalysts. Both for fundamental understanding and for rational reactor and process design, it is of vital importance to distinguish between thermal and non-thermal contributions. Therefore, we accurately monitor the temperature at multiple positions inside the catalyst bed *in operando* using a tailor-made fiber Bragg grating-based fiber optic sensor (FBG-FOS).

Experimental/methodology. We developed a tailored FBG-FOS to measure the temperature of the illuminated plasmonic catalyst bed at multiple positions: at the surface (0 mm), and at 0.15 mm, 0.30 mm and 0.50 mm depth. We applied this sensor for *in operando* temperature monitoring in the sunlight-powered reverse water gas shift reaction. We varied the irradiance, flow rate and feedstock composition and studied their effect on production rate, yield, selectivity, surface temperature and temperature gradient inside the catalyst bed. We applied a Au/TiO_2 nanocatalyst, which we prepared by deposition-precipitation of Au nanoparticles on TiO_2. We extensively characterized chemical composition, nanostructure and optical properties of this plasmonic catalyst.

Results and discussion. We successfully prepared a plasmonic Au/TiO_2 catalyst by deposition-precipitation of Au on anatase, and achieved a Au loading of 3.12% w/w (ICP-AES).[1] The average size of the Au nanoparticles was 1.6 nm (lognormal distribution), and their (111) lattice planes were perfectly alligned with the (101) TiO_2 planes. The catalyst displayed a strong plasmonic absorption in the visible, with a maximum in the wavelength range between 500 nm and 600 nm. We demonstrated that under illumination with sunlight (irradiance up to 14.4 $kW \cdot m^{-2}$), CO was produced at high selectivity of 98% without external heating of the reactor. In comparative dark experiments at similar catalyst bed temperature (~200°C), only CH_4 was produced. Under optimized conditions, we achieved a CO production rate of 429 $mmol \cdot g_{Au}^{-1} \cdot h^{-1}$ and reached an apparent quantum efficiency of 4.7%.[1] When studying the CO production rate as function of solar irradiance, we obtained an exponential relationship indicating the presence of a photothermal contributor. [1] To distinguish between photothermal heating and non-thermal contributors, we performed experiments using a tailored FBG-FOS temperature sensor for *in operando* temperature monitoring. We previously demonstrated this concept for off-line measurements only. [2]

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Bismuth-based perovskites as photocatalysts for amines oxidation

J. C. Lopes[1,2*], J. Albero[3], M. J. Sampaio[1,2], C. G. Silva[1,2], H. García[3], J. L. Faria[1,2]

[1]*LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*
[2]*ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*
[3] *Instituto Universitario de Tecnología Química CSIC-UPV Universitat Politècnica de València, Av. de los Naranjos s/n, 46022 Valencia, Spain*
[*] *joanacl@fe.up.pt*

Introduction. Hybrid halide perovskites appeared as a class of emerging semiconductors materials with broad application in the field of solar cells and, more recently, for CO_2 reduction, hydrogen production and organic synthesis using photocatalysis technology [1]. Unfortunately, the most efficient hybrid perovskites contain lead, a severe toxic disadvantage for its applicability. Thus, it is crucial to find non-toxic alternatives to replace lead from the perovskite structure while preserving its optical properties. Bismuth halide perovskites have attracted interest due to their photocurrent efficiency, low toxicity, and air stability.
Increased attention has been focused on the direct synthesis of imines through the oxidative coupling of benzylamines using sustainable technologies such as photocatalysis, owing to reduced energy consumption and a simplified process. This work reports an efficient procedure using bismuth hybrid perovskites as photocatalysts for oxidative coupling of amines to imines.
Experimental/methodology. $Cs_3Bi_2Cl_9$ (CBC) and $Cs_3Bi_2Br_9$ (CBB) perovskites were synthesized by mixing a certain amount of CsBr-to-$BiBr_3$ and CsCl-to-$BiCl_3$ precursors, respectively, using DMF as solvent at 60 °C under continuous stirring for 12 h. The photocatalytic efficiency of perovskite-based materials was evaluated using benzylamine (BZA) as subtract for N-benzylidenebenzylamine (BZI) synthesis. The reactions were performed under visible light irradiation.
Results and discussion. Different techniques were used to characterize the synthesized catalysts. The synthesized CBC and CBB photocatalysts match very well with the characteristic reflections in the X-ray diffraction pattern, indicating the high crystallinity of the samples. DRUV-Vis spectroscopy analyses revealed that all the materials exhibited a high absorbance band edge in the visible region. The calculated bandgap energies for CBC and CBB were 2.64 and 3.10 eV, respectively. The photocatalytic performance of the perovskites was evaluated in the oxidative coupling of BZA using CBB and CBC as photocatalyst.

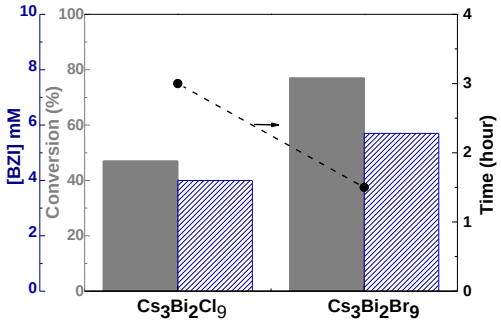

Figure 1- BZA conversion, BZI concentration (bars) and reaction time for maximum BZI production.

A maximum BZI concentration of 5.7 mM was attained after 1.5 hours for 77% conversion of BZA (Figure 1).

Acknowledgments
This work was financially supported by LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC). The authors also thank the project ClimActic (NORTE-01-0145-FEDER-000071), funded by European Regional Development Fund (ERDF) through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES. H.G. and J. A. thanks the financial support from the Spanish Ministry of Science and Innovation (Severo Ochoa CEX2021-1230-S, PDI2021-126071-OB-C21 and PLEC2021-7831), Generalitat Valenciana (Prometeo 2021-038 and MFA-2022-023), are gratefully acknowledged. J.A. also thanks the Spanish Ministry of Science and Innovation for a Ramon y Cajal research associate contract (RYC2021-031006-I). JCL acknowledges the PhD research grant from FCT, Ref. 2020.04651.BD. T.

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Plasma assisted photocatalytic non-oxidative coupling of methane over FeNi-layer double hydroxides

G. De Felice[1*], S. Li[1], F. Gallucci[1] and E. Rebrov[1,2]

[1]*Eindhoven University of Technology, Eindhoven, The Netherlands*
[2] *University of Warwick, Coventry, United Kingdom*
[*]*g.de.felice@tue.nl*

Keywords: layer double hydroxides, photocatalysis, methane activation, non-thermal plasma

Introduction. In the last decades, light-driven catalysis for methane activation has been object of intensive studies[1]. Amongst the different photocatalysts, layered double hydroxides (LDHs) are attracting attention as efficient visible light driven photocatalysts due to their unique layered structure, tunable band gap, high versatility in chemical composition, uniform distribution of metal ions and relatively low cost[2]. In this study, FeNi-LDHs were prepared and employed in plasma assisted photocatalytic non-oxidative coupling of methane in a planar dielectric barrier discharge (PDBD) reactor.

Experimental/methodology. FeNi-LDHs were synthesized by hydrothermal method at a pH of 7-12. Briefly, an aqueus solution containing desirable amounts of Ni and Fe precursors, hexamethylenetetramine and sodium hydroxide was stirred for 1 h at room temperature. Then, the suspension was transferred into a Teflon lined autoclave and placed in an oven at 393 K for 24 h. The catalyst was characterized with XRD, UV-Vis, SEM/EDX, N_2 chemisorption, and kinetic measurements under plasma, visible light, and plasma/visible light combination. The kinetic experiments were carried out in the reactor composed of a stainless steel electrode, and a transparent ITO electrode separated by a quartz dielectric layer. The catalyst was illuminated with a visible light using a set of LED with different wavelengths.

Results and discussion. The results establish a uniform distribution of Ni and Fe elements in the catalyst, and the mole ratio of Ni and Fe is close to the nominal ratio. The UV visible spectra of FeNi-LDHs synthesized at different pH are shown in Fig. 1.

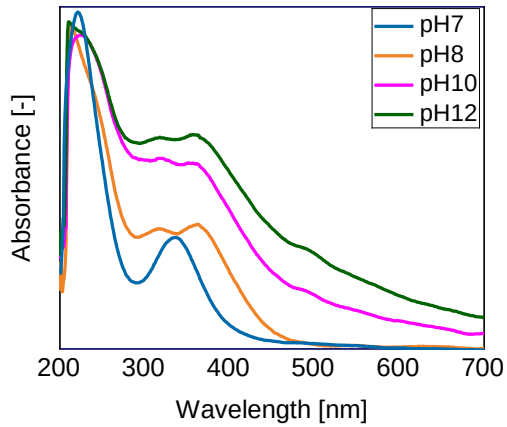

Figure 1. UV-vis spectra for samples at different pH.

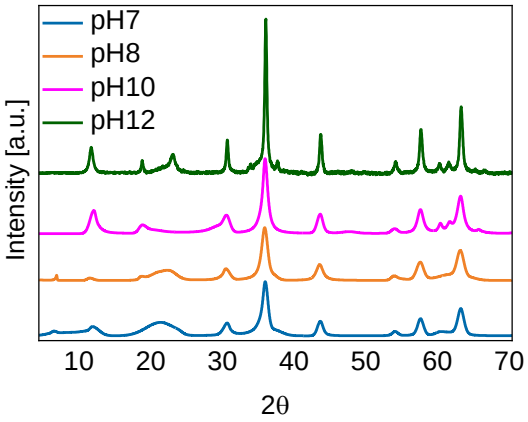

Figure 2. XRD pattern of NiFe-LDH prepared at different pH.

All the samples show a very strong UV absorption peak in the UV region (band centered at 215 nm). Samples obtained at pH>10 exhibit strong absorption characteristics in the full range from ultraviolet to visible and near-infrared light. As the pH increases, the absorption in the visible light region broadens due to a highly crystalline structure formed. The sample synthesized at pH=12 demonstrated the highest crystallinity. The XRD pattern of the synthesized FeNi-LDHs shows a lamellar structure with R3m rhombohedral symmetry (JCPDS card 22-0700)[3]. Different distributions of hydrocarbons were obtained over the catalysts.

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Photo-thermal catalysis as a tool to investigate the reverse water gas shift reaction over Cu/Al_2O_3

Kristijan Lorber[1,2], Jordi Sancho-Parramon[3], Janez Zavašnik[4], Iztok Arčon[2], Anže Prašnikar[1], Blaž Likozar[1] and Petar Djinović[1,2*]

[1]National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia
[2]University of Nova Gorica, Vipavska 13, SI-5000 Nova Gorica, Slovenia
[3]Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia
[4]Institute Jožef Stefan, SI-1000 Ljubljana, Slovenia
**petar.djinovic@ki.si*

Keywords: photo-thermal catalysis, reaction mechanism, *in-situ* spectroscopy

Introduction. The Reverse Water Gas Shift reaction (RWGS) is an attractive approach for CO_2 conversion to CO using renewable hydrogen[1], and could play an important role in the transition to sustainable, large-scale CO_2 utilization for fuel manufacture via syngas chemistry.[2] Photo-thermal catalysis is an emerging approach towards utilization of symbiotic effects of light (photon energy) and thermal energy to accelerate the catalytic turnover and influence selectivity.[3,4] Photo-thermal catalysis could have important consequences for enabling a more widespread use of solar irradiation to help drive catalytic reactions at mild conditions, and overcome conversion and/or selectivity limitations of equilibrium reactions.[5]

Experimental/methodology. A commercial γ-Al_2O_3 was used as a support to deposit between 5 and 14 wt.% copper. Structural analysis was performed using XRD, N_2 sorption, N_2O chemisorption, H_2-TPR, *in-situ* XAS and HRTEM techniques. *In-situ* UV-Vis and DRIFTS were used to analyze light-matter interactions and surface species during RWGSR in dark and under illumination. Catalytic tests with variable temperature, irradiance and wavelength dependent experiments were performed in fixed bed reactor.[5]

Results and discussion. The RWGS performance of Cu/γ-Al_2O_3 catalysts in thermally driven and photo-thermal RWGS reaction is notably different. When the reaction is driven by a combination of visible light (790mW/cm^2, which equals about 7 sun intensity) and thermal energy, the CO_2 rates were consistently lower compared to thermally driven reaction in dark. The linear correlation between irradiance and decreasing reaction rate suggested the rate attenuation is driven by a single photon process, and is not a temperature induced artefact. In photo-thermal mode, the Ea values were larger (~85 kJ/mol compared to ~67 kJ/mol in dark), suggesting light disrupts the energetically more favorable reaction pathway which is active in dark. Also, illumination of the catalyst can be used to steer selectivity away from methane (into CO), especially over catalysts with a higher copper content (9-14 wt.%) which contain larger Cu particles. The *in-situ* DRIFTS analysis of the Illuminated catalyst shows a substantial and only partly irreversible surface dehydroxylation, revealing the importance of OH groups in the RWGS pathway. There appears to be no correlation between formate and CO yield, identifying its minor active role in the RWGS pathway. This work provides a novel approach to manipulate the abundance, and analyze the role of different surface species with the capability to steer activity and selectivity in the RWGS reaction.

Acknowledgments
Slovenian Research Agency ARRS funding through program P1-0418 and projects J2-1726 and N2-0265. Dr. Damjan Lašič Jurković is kindly acknowledged for H_2-TPR and N_2O chemisorption analyses.

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New organic photocatalysts for homogeneous and heterogenous photooxidations in batch and flow reactors

S. Eeckhout,[1*] A-S. Léonard,[1] N. Body,[1] C. Lefebvre,[1] A. Y-H Tsai,[2] P. Bianchi,[2] J-C. Monbaliu,[2] O. Riant[1] and S. Hermans[1]

[1]*Institut IMCN - MOST, UCLouvain, Place Louis Pasteur 1, 1348 Louvain-la-Neuve, Belgium*
[2]*CITOS, ULiège, Quartier Agora, Allée du 6 août 13, 4000 Liège, Belgium*
[*]*sarah.eeckhout@uclouvain.be*

Introduction. The abounding environmental issues of our time have pushed sustainability at the forefront of scientific research. Due to the surging energy demand, many researchers are turning to clean and renewable resources such as solar power. In chemistry, light-driven processes have been blooming through photocatalysis, a valuable tool for implementing greener strategies. Ruthenium and iridium-based polypyridyl complexes are prominent organometallic photocatalysts but their rareness, elevated cost, and toxicity can be inconvenient. Alternatives, such as fully organic photocatalysts, have been researched and could constitute adequate replacements.[1] However, due to the homogeneous nature of these chromophores, recyclability remains an issue,. The aim of this project therefore consisted in the development of a recyclable and accessible photocatalytic system, applicable to fine organic synthesis, namely photooxidation steps.

Results and discussion. Based on benzophenazines investigated for photodynamic therapy,[2] a new set of organic chromophores were developed (Fig. 1). Their synthesis was achieved through a straightforward two-step pathway and photocatalytic activity was benchmarked by the photooxidation of citronellol.[3] The tested chromophore displayed excellent photocatalytic yields of up to 99 % in 2 hours, hence confirming its photocatalyst status. A theoretical study was also performed to reach a finer understanding of the molecule's properties as well as to establish a structure-activity relationship. It was found that photocatalysts with electron donating groups on their southern site (Fig.1, blue) tend to absorb at longer wavelengths, which is desirable for reaching lower energy activation.

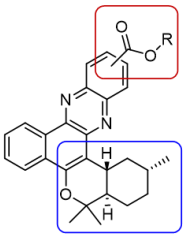

Figure 1. Organic chromophore.

Heterogenization was carried out using silica nanoparticles (SNPs) functionalized with primary amines. After screening different sizes, characterized by DLS and TEM, silica nanoparticles of 40 nm (Fig. 2) were found to be of ideal size as light scattering was minimized. The immobilization of the organic photocatalyst was successfully achieved through peptide coupling between the surface amines of the nanoparticles and the activated ester of the chromophore (located on the northern site: Fig.1, red). Quantification of the anchored chromophore was achieved by TGA and XPS was used to verify its unaltered presence on the surface. Solids with loads ranging from to 2 to 8 wt.% of photocatalyst were obtained through our method. The resulting silica-supported photocatalyst was tested over several runs using the same benchmark reaction as the homogeneous tests. Remarkable photocatalytic activity was observed as the heterogenized photocatalyst reached up to 97 % yields in overnight photooxidation runs and conserved similar activity for 4 cycles with only a slight decrease. The grafted chromophore also displayed improved resistance to photodegradation. These new photocatalysts are currently being extended to flow reactors. In homogeneous conditions, up to 95 % of conversion was observed with 1 min of residence time for the photooxidation of N-Carbobenzyloxy-L-methionine. This is a promising result as we look towards potentially implementing heterogeneous photocatalytic reactions in flow reactors. These findings attest the utility of heterogenizing homogeneous photocatalysts for obtaining greener catalytic systems.

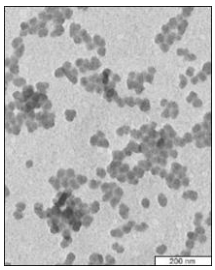

Figure 2. TEM images of 40 nm SNPs.

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Light-induced production of hydrogen peroxide from saccharides using carbon nitride immobilized on a 3D-printed structure

Maria J. Sampaio[1,2], Rita A. Borges[1,2], Marta F. Pedrosa[1,2], Yaidelin A. Manrique[1,2], Cláudia G. Silva[1,2], Adrián M.T. Silva[1,2], Joaquim L. Faria[1,2*]

[1]LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[2]ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

**Corresponding author: jlfaria@fe.up.pt*

Keywords: Photocatalysis; carbon nitride, visible light; GCN-T/3D-structure

Introduction. Hydrogen peroxide (H_2O_2) is an important commodity compound listed as one of the 100 most widely used worldwide [1]. Demand for sustainable energy and chemical synthesis has encouraged the scientific community to expand the concept of artificial photosynthesis that mimics nature to convert water and light energy into value-added products. Heterogeneous photocatalysis has been appointed as a promising alternative route for H_2O_2 generation due to its advantage of operating under mild temperatures and exempting the use of hazardous reagents [2]. The key to applying this technology lies in developing innovative catalysts and using sustainable resources to compete with the traditional industrial process of H_2O_2 production. Among the optical semiconductors applied in the field of photocatalysis, graphitic carbon nitride (g-C_3N_4) has revealed significant potential for H_2O_2 production using aqueous solutions in the presence of alcohols, such as 2-propanol, ethanol, and methanol [2]. Alternatively, saccharides as biomass derivatives may constitute a sustainable solution by acting as electron donors during the photocatalytic process.

Experimental/methodology. A bulk g-C_3N_4 synthesized by thermal condensation of dicyandiamide and post-treated at 500 ^{o}C (here labeled as GCN-T) [3] was used as a photocatalyst towards the production of H_2O_2 under visible light exposure. Saccharides, such as arabinose, cellobiose, fructose, and glucose, were used as sacrificial electron donors. Operational parameters, such as the effect of the initial concentration of the electron donor and the presence of ionic species, were investigated, aiming for the enhancement of H_2O_2 generation. Seeking a sustainable technological approach for H_2O_2 production, GCN-T was immobilized on a 3D printed structure prepared by additive manufacturing. In addition, synthetic water, mimicking the salinity of seawater, as well as natural seawater samples, was used.

Results and discussion. The results showed that the scavenging efficiency of the photogenerated holes rapidly increases with the number of –OH groups and differs as a function of the molecular structure of the sacrificial agents. Among the polyhydroxy compounds used, a high concentration of H_2O_2 was detected using cellobiose as the electron donor. When GCN-T was immobilized on the 3D structure, the photocatalytic system exhibited high efficiency and robust stability for H_2O_2 production. In addition, the GCN-T/3D-structure demonstrated promising results, revealing a superior apparent quantum efficiency at 412 nm compared with the results attained using GCN-T suspensions.

Acknowledgments

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Photo-themocatalytic CO_2 methanation over Ru nanoparticles supported on metal oxides

M. Imizcoz*, F. Almazán, I. Pellejero, L.M. Gandía

Institute for Advanced Materials and Mathematics (INAMAT²) - Public University of Navarra (UPNA), Pamplona-Iruña, Spain
**mikel.imizcoz@unavarra.es*

Keywords: Photo-thermal catalysis, Carbon dioxide, Sabatier reaction, Supported ruthenium nanoparticles

Introduction: The Sabatier reaction have undergone a revival in the last years due to its potential for the obtainment of CH_4 (synthetic fuel and hydrogen carrier), while depleting CO_2 responsible of greenhouse effect[1]. In this sense, photo-thermal catalysts have the potential of driving this reaction in gentle conditions, by exploding the whole sunlight spectrum in the form of heat and charge-carrier generation. Some well-known Sabatier catalysts, like supported Ru, have already reported higher activity under photo-thermal conditions[2], although a deeper understanding of the light-catalyst interaction is still needed.

Experimental/methodology: In this work, metallic ruthenium nanoparticles at a total loading of 2% have been deposited on different metal oxides (TiO_2-P25, TiO_2-Anatase, ZrO_2, CeO_2 and SiO_2) and fully characterized by ICP-AES, H_2-TPR, CO-Chemisorption, N_2-Physisorption, TEM, DR UV-Vis spectroscopy and XRD. Their catalytic activity has been tested in a commercial Harrick reactor with an additional thermocouple in the catalytic bed, under Sabatier reaction conditions. During the test the catalysts were exposed to 300W Xe lamp (AM 1.5G) illumination at a total irradiance of 0.3 W cm^{-1}, and the experiment was repeated without light for comparison.

Results and discussion: The synthesis yielded materials with metallic ruthenium nanoparticles smaller than 5 nm homogeneously dispersed, as verified by TEM (Figure 2) and H_2-TPR. All catalyst showed metal loadings close to the nominal value, confirmed by ICP-OES, and absorption in the whole UV-Vis spectrum. According to figure 1 $Ru_{0.02}$@TiO_2-P25 and $Ru_{0.02}$@ZrO_2 were the most active catalysts followed by $Ru_{0.02}$@CeO_2, while $Ru_{0.02}$@SiO_2 and $Ru_{0.02}$@Anatase yielded less conversion. All the materials were highly selective towards CH_4. The addition of light clearly improved the catalytic activity in all cases, being this enhancement most marked for $Ru_{0.02}$@ZrO_2 and $Ru_{0.02}$@TiO_2-P25. New catalytic tests are scheduled to confirm this tendency and shed light on the causes of the support effect observed.

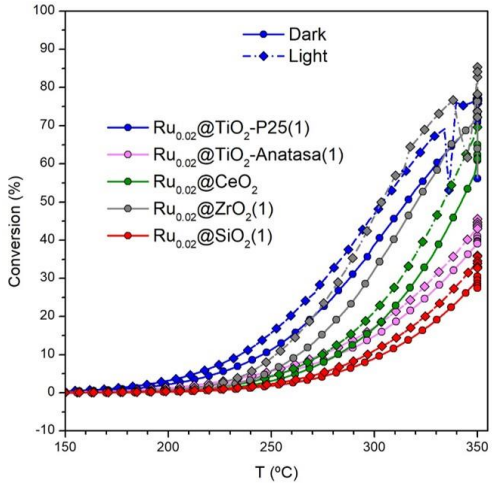

Figure 1. Catalyst activity during CO_2 methanation.

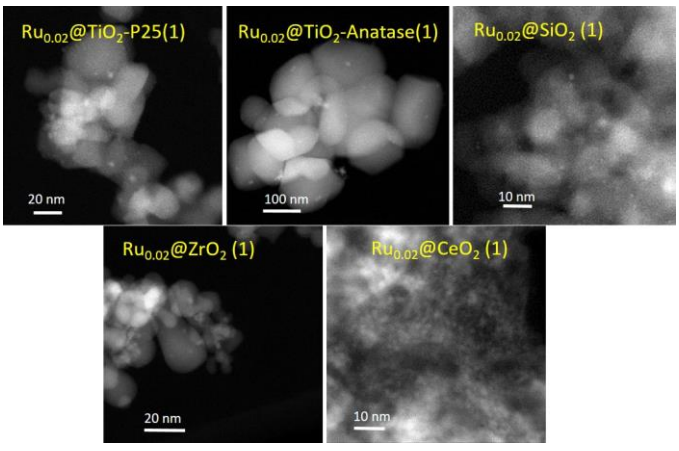

Figure 2. TEM micrographs of all the catalyst before reaction.

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TiO_2 decorated with metallic nanostructures for hydrogen production. Is the SPR involved in the mechanism of its activity?

A. Jakimińska[1,2*], K. Spilarewicz[1], W. Macyk[1*]

[1]*Faculty of Chemistry, Jagiellonian University, ul. Gronostajowa 2, 30-387 Kraków, Poland*
[2]*Doctoral School of Exact and Natural Sciences, Jagiellonian University, ul. Łojasiewicza 11, 30-348 Kraków, Poland*
[*]*anna.jakiminska@doctoral.uj.edu.pl, macyk@chemia.uj.edu.pl*

Introduction. Metallic nanostructures are widely used as the modifiers in photocatalysis. Most of the research reports the salutary influence of surface plasmon resonance (SPR) on the modified photocatalysts activity, especially in the visible light range [1-3]. Nevertheless, despite the fact that the presence of metallic nanostructures can be advantageous, the hot-electrons injection or plasmon induced resonance energy transfer processes are not very efficient. Moreover, activity of such materials under visible light irradiation is disputable. How then the presence of metallic nanostructures enhances the activity of modified materials?
Experimental/methodology. During this research, the influence of metallic nanostructures presence on the activity of titanium dioxide in hydrogen production from methanol oxidation and pure water splitting was examined. Metallic nanostructures were photodeposited at the TiO_2 surface and the hydrogen evolution was monitored using gas chromatography. Additionally, measurements of spectral, photoelectrochemical and spectroelectrochemical properties of modified materials were performed.
Results and discussion. Received results indicate that the influence of metal type and the structures size are the most important in terms of enhanced activity, whereas the presence of SPR phenomenon is not. Therefore, implementing of SPR in the mechanisms of activity of metallic nanostructures decorated materials should be reconsidered.

Acknowledgments
Authors would like to acknowledge National Science Centre in Poland for financial support within Solar-Driven Chemistry project (2019/01/Y/ST5/00027).

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Reductive production of H_2O_2 over metal-free WO_3 Photocatalyst at elevated temperatures

K. Kamitani[1], A. Tanaka[2], H. Kominami[2]*

[1]*Molecular and Material Engineerring, Kindai University, Higashiosaka, Osaka, Japan*
[2]*Department of Applied Chemistry, Kindai University, Higashiosaka, Osaka, Japan*
**hiro@apch.kindai.ac.jp*

Keywords: photocatalyst, hydrogen peroxide, tungsten oxide

Introduction. Hydrogen peroxide (H_2O_2) attracts attention in various fields in synthesis of pharmaceuticals and organic functional materials, and recently as an energy carrier [1] that can replace hydrogen. It is also becoming increasingly valuable as a green chemical, since the only decomposition products of H_2O_2 are water and oxygen (O_2). However, the anthraquinone method [2], the current industrial manufacturing method, requires a multi-step synthesis process, toxic organic solvents, and explosive gases. Therefore, there is a need for a synthetic method that is simpler and has less environmental impact, and the photocatalytic method is being studied as one of the promising methods [3]. H_2O_2 can be produced over various photocatalysts by reduction of O_2 by photogenerated electrons. Since H_2O_2 decomposes by UV light, visible light-driven photocatalysts such as tungsten(VI) oxide (WO_3) are favorable. In addition, the position of the conduction band more positive than the potential of one electron reduction of O_2 makes the H_2O_2 production advantageous. Here we achieved H_2O_2 production by two electron reduction of O_2 ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$) in an aqueous 2-propanol (IPA) suspension of metal-free WO_3 photocatalyst. We also found thermal acceleration of the photocatalytic reaction, i.e., the rate of H_2O_2 production greatly increased at slightly elevated temperatures. This study aims to analyze the mechanism in this reaction and to achieve more efficient H_2O_2 production.

Experimental/methodology. WO_3 powder (50 mg) was suspended in a 90 vol% 2-propanol-H_2O (5 mL) in a test tube and the gas phase was placed with O_2. The test tube in a glass-type water bath kept at various temperatures was irradiated with visible light ($\lambda > 400$ nm) using a Xe lamp equipped with an L-42 cut filter. After the reaction, O_2 in the gas phase and acetone in the liquid phase were analyzed by gas chromatography, while the H_2O_2 in the liquid phase was colored by Trinder's reagent and analyzed spectrophotometrically.

Results and discussion. Figure shows effects of the reaction temperature on the yield of H_2O_2 after visible light irradiation for an hour. The yield of H_2O_2 was very small at 27 °C. We found that the yields drastically increased with an elevation of the reaction temperature and, finally, the yield reached 80 μmol at 60°C, which corresponded to 16 mmol L^{-1}. These results indicate that an activation energy barrier exists in the O_2 reduction process and/or the oxidation process. In the photocatalytic production of H_2O_2, oxidation of IPA by positive holes simultaneously occurred, resulting in formation of acetone ($IPA + 2h^+ \rightarrow$ acetone $+ 2H^+$). To analyze this reaction in detail, electron utilization efficiency (EUE) was calculated and plotted in Figure. If two electron reduction of O_2 and oxidation of IPA occur stoichiometrically, the value of EUE should be unity. However, the values of EUE were 20-25% at any temperatures, suggesting that self-decomposition of H_2O_2 and/or oxidation of IPA by H_2O_2 occurred.

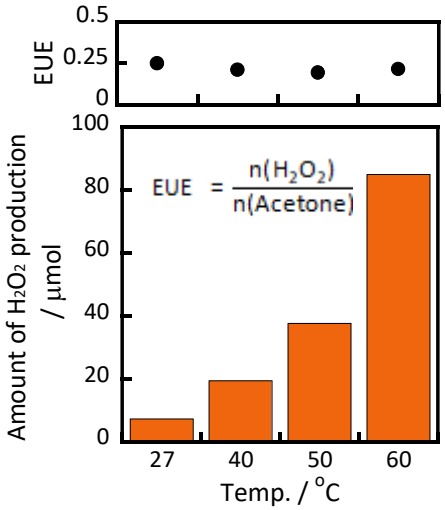

Figure Effects of reaction temperature on production of H_2O_2 and electron utilization efficiency over WO_3 photocatalyst in 90 vol% 2-propanol under irradiation of light from Xe lamp with L-42 cut-filter for 1 h.

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Breaking selectivity limits in the photocatalytic oxidation of methane to formic acid: Contribution of thermocatalysis

D. Hu[1], A. Addad[2], K. Ben Tayeb[3], V. V. Ordomsky[1]* and A. Y. Khodakov[1]*

[1]*Université Lille, CNRS, Centrale Lille, University Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, 59000 Lille, France*

[2]*Université Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, 59000 Lille, France*

[3]*Université Lille, CNRS, UMR 8516 – LASIRE – Laboratoire de Spectroscopie pour les Interactions, la Réactivité et l'Environnement, 59000 Lille, France*

Vitaly.Ordomsky@univ-lille.fr; Andrei.Khodakov@univ-lille.fr

Keywords: photocatalysis, methane activation, cascade process, formic acid, high selectivity

Introduction. Direct oxidation of methane into value-added fuels and chemicals remains a major challenge in modern science [1, 2]. Formic acid is one of the most promising platform-molecules for hydrogen storage, low-temperature membrane fuel cells and synthesis of platform molecules. Photocatalysis proposes an attractive route for methane partial oxidation to value added chemicals under mild conditions. The radical mechanism of methane photocatalytic oxidation often restricts the selectivity to the target products. In this paper, we propose a strategy to break the conventional limitations of methane photocatalytic oxidation by adding a thermo-catalyst and conducting the whole process in a one-pot reactor at ambient temperature.

Experimental/methodology. The cesium salt of phosphotungstic acid (CsPW) was prepared by mixing heteropolyacid hydrate aqueous solution with the stoichiometric amount of $CsNO_3$ aqueous solution. For preparation of CsPW-TiO_2 photocatalyst, CsPW was mechanically mixed with a necessary amount of TiO_2. The catalysts were characterized by XRD, UV, STEM, photoluminescence and EPR. A commercial 230 mL batch photoreactor equipped with a quart window on the top was used for photocatalytic methane oxidation reaction tests. In the photo- thermo-catalytic experiments, the photoreactor was equipped with a sand filter to isolate CsPW-TiO_2 photocatalyst and Ru/Al_2O_3

Results and discussion. Methane photocatalytic oxidation results in a mixture of C_1 oxygenates (Fig. 1a). The selectivity of methane oxidation to formic acid is dramatically improved in the proposed photo-thermo-catalytic cascade process. The process involves a photocatalyst prepared from caesium salt of phosphotungstic acid mixed with titania and an alumina supported ruthenium catalyst. In the photo-thermo-catalytic process (Fig. 1b), a yield of formic acid over 5000 µmol g^{-1} and a selectivity of 85% were achieved. CO_2 is the only gaseous compound of methane oxidation. Optimization of catalyst structure and reaction conditions allows a one pot synthesis of HCOOH solution from methane with a concentration of 1.1 mmol L^{-1}. Our findings offer valuable guidance for the direct and highly selective methane oxidation to HCOOH in water using O_2 as an oxidant.

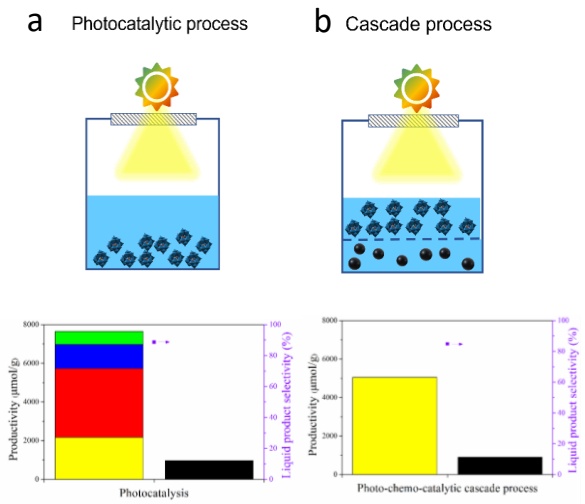

Fig. 1. Methane oxidation in photocatalytic (**a**) and cascade photo-thermo-catalytic processes (**b**).

Acknowledgments

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Glycerol as an excellent hydrogen and electron source for photocatalytic hydrogenation of nitrobenzene in water

H. Kominami[1,*], K. Onogi[2], A. Tanaka[1]

[1]*Department of Applied Chemistry, Kindai University, Higashiosaka, Osaka, Japan*
[2]*Molecular and Material Engineering, Kindai University, Higashiosaka, Osaka, Japan*
[*]*hiro@apch.kindai.ac.jp*

Keywords: Glycerol, hydrogenation, photocatalyst

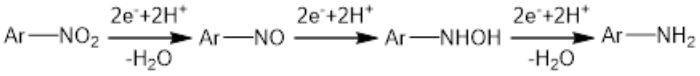
Introduction. Hydrolysis of fats and oils with alkalis such as sodium hydroxide and potassium hydroxide (saponification) produces glycerol and salts of higher fatty acids [1]. The salts of higher fatty acids have been used as soaps and surfactants for a long time because the anions of higher fatty acids show osmosis, emulsification, and dispersing action. Recently, conversion of fats and oils to methyl esters (biodiesel fuels) with methanol via an ester exchange reaction has been extensively investigated from the viewpoint of reduction in consumption of fossil fuels and utilization of biomass as carbon-neutral resources [2]. In both saponification and ester exchange reaction of fats and oils, glycerol is produced as a by-product. Glycerol is harmless to the human body and is used as a sweetener and a moisturizer in cosmetics. However, a large amount of energy is required to recover glycerol from aqueous wastes emitted from the soap production process due to its high solubility in water and high boiling point (290°C). In this study, we used glycerol as an electron and hydrogen source for photocatalytic hydrogenation of 4-nitrobenzenesulfonic acid (4-NBS) to 4-aminobenzenesulfonic acid (4-ABS) in an aqueous suspension of TiO_2.

Experimental/methodology. TiO_2 powder was suspended in 5 cm^3 of water containing 4-NBS (typically 50 µmol) and glycerol (typically 450 µmol) in a Pyrex test tube (18ϕ × 180 mm). After replacing the gas phase with argon, the test tube was sealed with a rubber septum and then photoirradiated at 20°C with the high-pressure mercury lamp (λ> 300 nm) under continuous stirring.

Results and discussion. Figure shows the time course of the photocatalytic hydrogenation of 4-NBS in an aqueous suspension of TiO_2 (25 mg) in the presence of glycerol (450 µmol). Just after photoirradiation, the amount of 4-NBS decreased and was no longer detected, while the amount of 4-ABS increased and the yield reached 95% at 2.5 h. The apparent quantum yield was roughly estimated to be ca 10%. As Figure 4 also shows, CO_2 was produced as the oxidation product and the final amount was 10 µmol. These results mean that oxidation stops when 4-NBS to be reduced is consumed. Ideal mineralization of glycerol to CO_2 is shown in Equation:

$$C_3H_5(OH)_3 + 3H_2O \rightarrow 14e^- + 14H^+ + 3CO_2.$$

According to the stoichiometry, 47 µmol of electrons (= (10/3) × 14) was provided for the reduction (hydrogenation) of 4-NBS. However, production of 45 µmol of 4-ABS requires 270 µmol of electrons (= 45 × 6) because conversion of 4-NBS to 4-ABS is a 6-electron process as shown below.



The large gap between yields of CO_2 and 4-ABS indicates that a large amount of a partial oxidation product(s) of glycerol was present in the liquid phase.

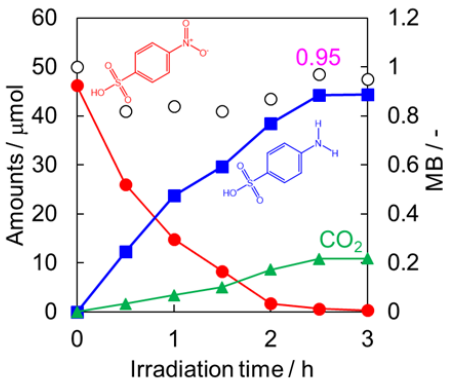


Figure Time courses of amounts of 4-NBS (●), 4-ABS (■), CO_2 (▲) and MB (○) in an aqueous suspension of TiO_2 (25 mg) in the presence of glycerol (450 µmol) under irradiation of UV light.

Acknowledgments

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Mechanistic study of glucose photoreforming over TiO_2-based catalysts for H_2 production

Lan Lan[1,*], Christopher Hardacre[2,*]

[1, 2] *The University of Manchester, Manchester, United Kingdom*
[*] *lan.lan@manchester.ac.uk (L. L.), c.hardacre@manchester.ac.uk (C.H.)*

Introduction.

Glucose is a key substrate proposed as the main intermediate in cellulose photoreforming for H_2 production. However, the mechanism of glucose formation in cellulose photoreforming and the mechanism of glucose photoreforming over TiO_2-based catalysts are currently not well understood [1]. The reaction pathways of glucose photoreforming have predominantly been determined from analysis of gas phase and liquid products. As the nature of adsorbed species on the catalyst surface could influence the oxidising species and reaction pathway, determination of adsorbed species on the catalyst surface from an aqueous solution, is an important consideration in understanding the photoreforming mechanism. Attenuated total reflectance infrared (ATR-IR) spectroscopy has been utilised to study the liquid-solid interface to probe adsorption on a catalyst surface (dark adsorption [2]) and also under *in-situ* conditions with irradiation of UV light [3]. Therefore, detailed product analysis combined with in-situ ATR-IR spectroscopy under UV irradiation has potentials to provide inforamtion for further understanding of glucose photoreforming mechnism over TiO_2-based catalysts.

Experimental/methodology.

Detailed product analysis of the system was performed by liquid and gas chromatography. An *in-situ* ATR-IR spectroscopy of m-TiO_2 (*i.e.,* mixed phase of 85% anatase and 15% rutile) and Pt/m-TiO_2 under UV irradiation was carried out to probe the species adsorbed on the surface of the catalyst during the photoreforming of glucose. In addition, isotope mass spectrometry was also employed to study the origin of H_2 in glucose and formic acid photoreforming over Pt/m-TiO_2 catalysts.

Results and discussion.

This work presents a mechanistic investigation of glucose photoreforming over TiO_2 and Pt/m-TiO_2 catalysts. Analysis of the intermediates formed in the photoreforming of glucose confirmed the α-scission mechanism of glucose oxidation forming arabinose (C_{n-1} sugar) and formic acid in the first oxidation step. The selectivity to sugar products and formic acid differed over Pt/TiO_2 and TiO_2 with lower selectivity to formic acid observed over Pt/TiO_2 attributed to enhanced adsorption/conversion of formic acid over Pt/TiO_2. *In-situ* ATR-IR spectroscopy of glucose photoreforming showed molecular formic acid and formate to be present on the surface of both catalysts at low glucose conversions, which suggests formic acid oxidation could dominate surface reactions in glucose photoreforming. Further *in-situ* ATR-IR of formic acid photoreforming showed Pt-TiO_2 interfacial sites to be key for formic acid oxidation as TiO_2 was unable to convert adsorbed formic acid/formate. Isotopic studies of the photoreforming of varied concentrations of formic acid in D_2O showed that the source of the protons reduced to H_2 at Pt particles, was determined by the relative surface coverage of adsorbed water and formic acid.

Acknowledgments

The authors would like to acknowledge the EPSRC-funded Supergen Bioenergy Hub 2018 (EP/S000771/1) for funding this research. UK Catalysis Hub is kindly thanked for resources and support provided via our membership of the UK Catalysis Hub Consortium and funded by EPSRC grants: EP/R026939/1, EP/R026815/1, EP/R026645/1 and EP/R027129/1.

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The influence of carbon spheres addition on photoactivity of TiO_2 and ZnO

Antoni W. Morawski[1*], Katarzyna Ćmielewska[1], Ewelina Kusiak-Nejman[1] , , Marcin Gano[2], Iwona Pełech[1], Joanna Kapica-Kozar[1] and Urszula Narkiewicz[1]

[1]*Department of Inorganic Chemical Technology and Environment Engineering, Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology in Szczecin, Pułaskiego 10, 70-322 Szczecin, Poland*

[2]*Department of Organic Chemical Technology and Polymer Materials, Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology in Szczecin, Pułaskiego 10, 70-322 Szczecin, Poland*

[*]*Antoni.Morawski@zut.edu.pl*

Keywords: photocatalysis, titanium dioxide, zinc oxide, carbon spheres, carbon dioxide reduction

Introduction. CO_2 photoreduction into valuable products is one of the most promising methods of fighting dangerous climate changes. TiO_2 is the most commonly used photocatalyst. It shows high activity, especially when two phases are combined [1,2]. Also, ZnO is considered a material with similar properties. Relatively low production costs and non-toxicity characterize both of them. On the other hand, carbon spheres show excellent CO_2 adsorption properties and high surface area (S_{BET}). Thanks to this, they can improve the photocatalytic properties of TiO_2 and ZnO since the ability of CO_2 adsorption is crucial in photocatalytic carbon dioxide reduction. The study aimed to achieve a synergistic effect of materials containing photocatalysts and carbon spheres by combining the two components with specific properties.

Experimental/methodology. Materials tested in photocatalytic processes contained P25 type TiO_2 (AEROXIDE® TiO_2 P25, Evonik Industries AG, Germany), ZnO with particle size <100 nm (Sigma-Aldrich, USA), and carbon spheres (CS). The CS/TiO_2 and CS/ZnO mixtures were prepared using a microwave-assisted solvothermal reactor (Ertec, Poland), as described in a publication [3]. The photocatalytic tests were performed in a liquid-phase reactor with a 150 W medium-pressure mercury lamp TQ150 Z3 (Heraeus, Germany). The suspension of 200 mg of the tested sample in 0.2M aqueous NaOH solution was saturated with pure CO_2 and irradiated with UV light for 6 h. The products of CO_2 photoreduction were analyzed using a Master GC chromatograph (DANI Instruments, Italy) with micro-packed Shincarbon ST 100/120 column, TCD, and FID detectors. The carrier gas was argon. The H_2, CO and CH_4 amounts were calculated based on the calibration curve.

Results and discussion. The experiments were carried out to evaluate the photocatalytic activity of two groups of materials containing TiO_2 and ZnO by adding carbon spheres in the amount of 0.05-1.00 g of CS per 1 g of TiO_2/ZnO in CO_2 photoreduction. In the gas phase, the identified products of this process were hydrogen, carbon monoxide and methane. Based on the results, it can be concluded that materials containing TiO_2 exhibited slightly better activity than those with ZnO. Moreover, adding carbon spheres to titanium dioxide improved its photocatalytic activity towards carbon monoxide production. However, regardless of the photocatalyst, the main product was carbon monoxide. It can also be concluded that a minor addition of carbon spheres (0.10 g) was more efficient in the case of TiO_2. In turn, better results were obtained using zinc oxide for the mixture containing a high amount of carbon spheres (1.00 g).

Acknowledgements

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A $Pt/TiO_2/SiO_2/Si$ structured microreactor for the photogeneration of H_2

J. Llorca[1*], D. Vega[2], L. Soler[1*], A. Rodríguez[2*]

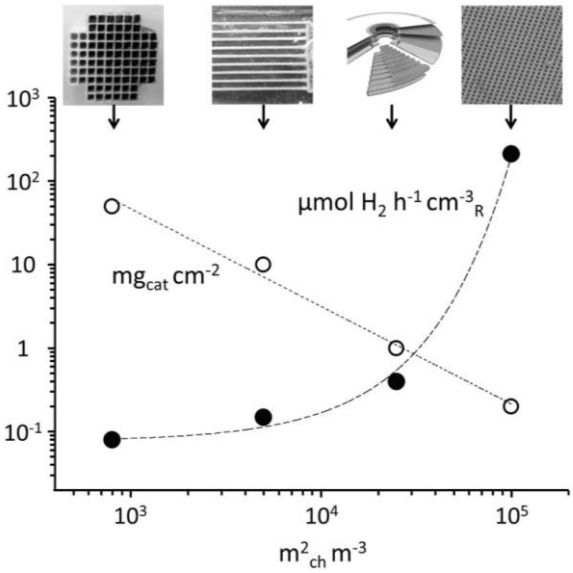
[1]*Department of Chemical Engineering and Institute of Energy Technologies, Universitat Politècnica de Catalunya, UPC-EEBE, Barcelona, Spain*
[2]*Department of Electronic Engineering, Universitat Politècnica de Catalunya, UPC, Barcelona, Spain*
[*]*jordi.llorca@upc.edu*

Keywords: hydrogen, microreactor, photocatalysis

Introduction. The photoproduction of H_2 represents one of the most desired routes to obtain renewable hydrogen. However, the H_2 photoproduction rates reported so far are too low for practical application. Whereas there is an impressive number of works related to the design of photocatalytic materials to increase the efficiency of the photoprocess, less attention has been paid to the proper design of photocatalytic devices [1-3]. Obviously, no matter how good a photocatalyst is, the overall hydrogen yield will be strongly limited if a proper mass and photon transfer to the photocatalyst is not attained. Therefore, both the photocatalyst and the photoreactor are equally important to guarantee a suitable operation.

Experimental/methodology. Photoassisted electrochemical etching was used to prepare silicon micromonoliths with straight, parallel channels of 2 μm arranged in a square lattice with a periodicity of 4 μm side over ⟨100⟩ n-type float-zone silicon. The microchannels were oxidized at 1373 K to partially transform Si into SiO_2. Titanium(IV) isopropoxide was forced to pass through the microchannels by applying a pressure difference of ca. 75 kPa. With this method, the hydroxyl groups of SiO_2 reacted with the titanium precursor to form surface titanium alkoxide groups, which were subsequently calcined at 723 K to form a compact TiO_2 layer over SiO_2. The $TiO_2/SiO_2/Si$ structure was decorated with Pt (0.77 wt.%) using an aqueous solution of $(NH_3)_4Pt(NO_3)_2$. The photocatalytic tests were performed in a tubular glass photoreactor. A gaseous reactant mixture of $EtOH:H_2O$=1:10 (molar) was forced to pass through the channels of the photocatalytic microreactor (GHSV=100,000 h^{-1}), which were illuminated at 365±5 nm (80 mW cm^{-2}). The outlet of the photoreactor was connected on-line to a gas chromatograph.

Results and discussion. The H_2 production rates as a function of the photoreactor volume (μmol H_2 h^{-1} cm^{-3}_R) and the photocatalyst loading normalized to the surface area (mg_{cat} cm^{-2}) of various microreactors are plotted against the specific contact area (m^2_{ch} m^{-3}) [4]. The fabulous rate of H_2 production on a reactor volume basis recorded with the macroporous silicon photocatalytic device (212 μmol H_2 h^{-1} cm^{-3}_R) is directly related to its high specific contact area (10^5 m^2_{ch} m^{-3}). There is an inverse trend between the specific contact area and the photocatalyst loading normalized to the surface area. As the number of channels increases and their diameter decreases, there is more contact area available and the thickness of the photocatalyst layer progressively decreases. This does not result in a decrease of the photocatalytic performance because photon absorption takes place only in the first micrometers of the photocatalyst coating.



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An Ab-Initio Study of Metal Oxo-Trimers Nanoporous MOF Building Units for the Catalytic Conversion of CO_2 to Methanol

Pengbo Lyu[1*,2], Guillaume Maurin[2*]

[1] *Hunan Provincial Key Laboratory of Thin Film Materials and Devices, School of Materials Science and Engineering, Xiangtan University, Xiangtan 411105, China*
[2] *ICGM, Université Montpellier, CNRS, ENSCM, Montpellier 34293, France*
[*] *Corresponding Author's E-mail address: pengbo.lyu@xtu.edu.cn (P. Lyu); guillaume.maurin1@umontpellier.fr (G. Maurin)*

Keywords: Metal-organic frameworks, Coordinatively unsaturated metal sites, CO_2 reduction, Catalysis, Molecular simulation, Understanding of mechanism, Rationalization, Prediction.

Introduction. (Photo)electrochemical driven CO_2 reduction becomes a promising way for both greenhouse gas mitigation and carbon-resource utilization which can provide renewable fuels with no net in-creases of CO_2. However, (photo)electrochemical CO_2 reduction requires multiple step transfers of protons and electrons generally associated with high energy barriers that require high overpotentials. Therefore, seeking catalysts with low overpotential is crucial to achieve efficient (photo)electrochemical CO_2 reduction. To this end, tremendous efforts have been devoted to exploring efficient catalysts for (photo)electrochemical CO_2 reduction, with particular attention given to Metal-organic frameworks (MOFs). MOFs containing metal oxo-trimer nodes with the chemical composition $M_3^{3+}(\mu_3\text{-}O)(X^-)(RCOO)_6$ (mono-metallic) or $(M_2^{3+}M'^{2+/3+}(\mu_3\text{-}O)(X^-)(RCOO)_6$ (bi-metallic) (M and M'=metal, X=counter-anion present to maintain charge neutrality in the case of all metal are 3+ and R=organic group of the linker) as secondary building units (SBUs) could be candidates for an effective catalytic CO_2 reduction, including MIL-88B(Fe),[1] MIL-101(Fe)[1], MIL-101(Cr)[2] and PCN-250-Fe_2M'(M=Fe, Mn, Zn, Ni, Co)[3] as they show catalytic activity for various (photo)electrocatalytic reactions. The identification of the optimum metal oxo-trimer nodes to be incorporated in the MOF framework is of utmost importance to design a catalyst with outstanding performance for (photo)electrochemical CO_2 reduction.

Experimental/methodology. All cluster optimizations were carried out using the unrestricted B3LYP exchange-correlation functional with the Gaussian 09 program suite. The oxo-trimer based cluster with terminal phenyl ring saturated by hydrogen atoms is in line with what has been reported previously in a number of theoretical catalysis investigations of MOF containing this oxo-trimer. The TZVP basis set was employed for all non-metal atoms; all metal atoms were treated by the LANL2DZ basis set. The DFT-D3 method was used to include the dispersion correction. These DFT calculations were combined with the computational hydrogen electrode (CHE) approach to investigate the CO_2 reduction mechanism.

Results and discussion. Employing density functional theory calculations, we explore the reaction mechanisms and activities for a series of metal oxo-trimer nodes within MOFs for catalytic CO_2 reduction to methanol. We first demonstrate that all investigated systems fulfill the thermodynamic requirement for CO_2 reduction regardless of pH value. Then we investigated the minimum energy pathways for CO_2 reduction over Fe-only system with experimentally proved activity as a benchmark. In comparison with Fe (II), Co(II) and Ni(II) substitution show equivalent or even better activity while Ni(II) is the most active one, whereas Cu(I), Cu(II), Zn(II), Cd(II), Ti(III), Y(III) and Ce(III) show poorer performance. Finally, we found that the stability of *COOH is a reliable descriptor to rank the catalytic activity and the origin is analyzed. Our computational efforts not only deliver a fundamental understanding of CO_2 reduction process over CUSs in MOFs, but also provide theoretical guidance for rational design of highly active catalysts for (photo)electrochemical CO_2 reduction based on MOFs containing metal oxo-trimer nodes.

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Low-temperature NH_3 decomposition using photo-thermal catalysis

Diego Mateo[1*], Angel Sousa[1], Luis Garzon-Tovar[1], Natalia Morlanes[1], Juan Carlos Navarro[1], Xinhuilan Wang[1], Kevin Brennan[2], Max Garcia-Melchor[2], Javier Ruiz-Martinez[1], Jorge Gascon[1*]

[1]*KAUST Catalysis Center, Thuwal, Saudi Arabia*

[2]*Trinity College Dublin, Dublin, Ireland*

[*]*diego.mateo@kaust.edu.sa*

Introduction. By virtue of its high volumetric energy density, well-defined distribution infrastructure and the possibility to obtain CO_x-free hydrogen (H_2) from its decomposition, ammonia (NH_3) is considered a key energy carrier in future neutral-carbon energy systems.[1] Unfortunately, the use of this carrier has been limited by the absence of an efficient NH_3 decomposition process. Photo-thermal catalysis, a hybrid approach that combines both thermal and non-thermal contributions of light, has showed a great potential to drive chemical reactions using sunlight as unique energy source.[2] In this work, we demonstrate for the first time the use of a MOF-derived photo-thermal catalyst to perform the NH_3 decomposition reaction at low temperatures and high conversion rates.

Experimental/methodology. Catalyst was obtained from the controlled pyrolysis under inert atmosphere of a metal-organic framework precursor. We studied the photo-thermal NH_3 decomposition under continuous flow configuration using a commercial Harrick cell equipped with a quartz window. The catalyst was loaded into the reactor system and it was irradiated from the top using a 300 W Xe lamp. The temperature was monitored with a thermocouple located a few mm below the catalyst surface and the evolved gases were quantified using a GC directly connected to the outlet of the reactor.

Results and discussion. As it can be seen in **Figure 1**, independently on the weight hour space velocity (WHSV), both the ammonia conversion and the temperature of the photocatalyst increased upon exposure to light until reaching a steady state. At 20000 mL g^{-1} h^{-1}, the catalyst reached a temperature of 300 °C and a 55 % NH_3 conversion, which translated into a H_2 production rate as high as 653 mmol H_2 g^{-1} h^{-1}. Indeed, at the lowest WHSV of 1000 mL g^{-1} h^{-1}, our system was able to decompose NH_3 at nearly full conversion (~80 %). Additional blank experiments under dark conditions displayed negligible NH_3 decomposition rates, thus indicating that the synergy between light and heat is crucial to enhance the catalytic activity towards NH_3 conversion. To the best of our knowledge, this is the first example of the use of a MOF-derived catalyst for the efficient photo-thermal NH_3 cracking reaction under continuous flow configuration at high conversion rates.

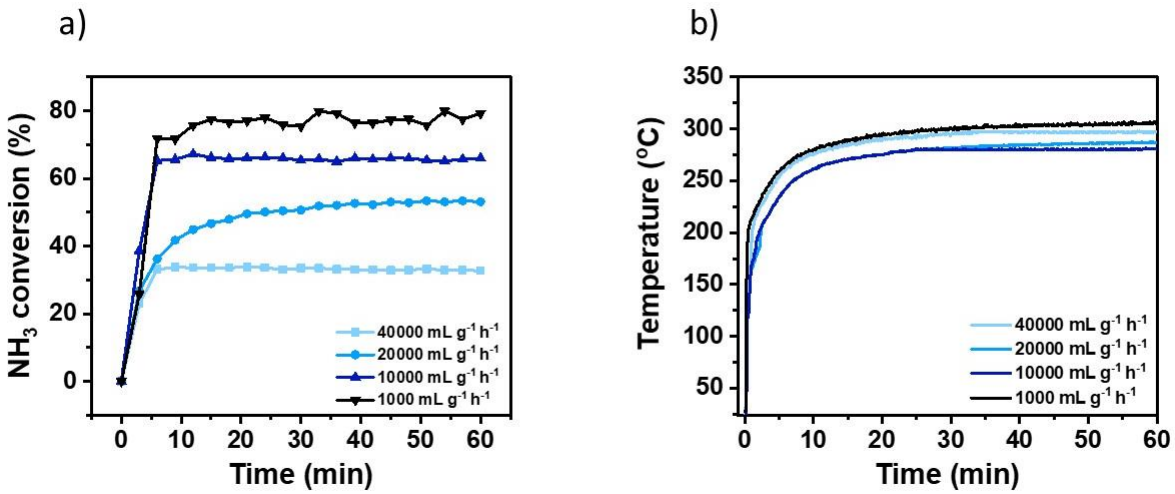

Figure 1. a) Photo-thermal NH_3 decomposition under different WHSV. b) Temperature profile of the catalyst under reaction conditions.

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PHOTOREFORMING OF BIOMASS SUBSTRATES WITH NON-NOBLE METAL/TiO_2 PHOTOCATALYSTS

M. Bouchabou, A. Brocani-Pasino, S. Belda-Marco, M.C. Román-Martínez, M.A. Lillo-Ródenas*

MCMA research group, Department of Inorganic Chemistry and Materials Institute (IUMA). Faculty of Sciences. University of Alicante, Alicante, Spain

****mlillo@ua.es***

Keywords: Lignocellulosic biomass, photoreforming, copper and nickel co-catalysts, hydrogen.

Introduction

Hydrogen is a potential alternative to fossil fuels because it is a clean, efficient, and renewable energy source. Producing H_2 via photochemical routes, more specifically by water splitting (WS), is a promising avenue. To overcome the disadvantage of the low efficiency of WS, catalytic photoreforming using a sacrificial agent in the reaction medium is an interesting approach [1]. In this regard, the present study focuses on verifying the potential of different types of biomass-derived-substrates as sacrificial agents in photocatalytic reactions for enhancing H_2 production (photoreforming reactions) using Metal/TiO_2. The substrates include local almond shell waste (**AS**), α-cellulose (**C**, Sigma-Aldrich), and a liquid residue from the process of activated carbon preparation by hydrothermal treatment of **AS** in 25 wt.% H_3PO_4 (**HMAS-L**).

Experimental/methodology.

Almond shell (**AS**) and α-cellulose (**C**) were mechanically pretreated (milled) in a planetary ball mill for reducing the particle size to increase their reactivity, leading to **MAS** and **MC** (from milled **AS** and **C**, respectively). **MAS** and **MC** were characterized by elemental analysis, proximate analysis, and XRD. The total organic carbon (TOC) content of **HMAS-L** was analysed as well. The photocatalysts used were the commercial P25 TiO_2 (Degussa) and MP25 (M: Cu or Ni, 1 wt. %) samples [2], that were prepared by impregnation with aqueous solutions of $Cu(NO_3)_2{\cdot}3H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ (both Panreac). The **1NiP25** and **1CuP25** photocatalysts were used without a previous reduction treatment and were characterized using XRD, ICP-OES, TEM, and XPS. Photocatalytic tests were conducted in a cylindrical glass reactor (Heraeus UV-RS-2) with a UV lamp (TQ 150-undoped, 47 W, λmax=365 nm), using a certain amount of substrate (**MAS, MC**, or **HMAS-L**), distilled water up to 500 mL, stirring in flowing He (30 mL/min) and 5 h illumination time. The generated gases were continuously analysed by mass spectrometry. Photodegradation of the 3 substrates (no catalyst), and water splitting tests were also carried out.

Results and discussion

Characterization of the solid substrates shows that **MAS** is richer in carbon and fixed carbon than **MC**, and that both substrates have low crystallinity. The total organic carbon (TOC) analysis of **HMAS-L** reveals that it contains a large amount of dissolved organic matter (20850 mg/L). ICP-OES analysis has confirmed that the metal content in **1CuP25** and **1NiP25** is very close to the nominal one. In both cases, TEM shows a good metal dispersion, and mean particle sizes lower than 3 nm. XRD patterns only exhibit the characteristic peaks of TiO_2 (P25), and XPS data show that the main species are Cu (I/0) in **1CuP25** and Ni (II) in **1NiP25**. The photochemical results highlight that the H_2 production largely depends on the substrate and photocatalyst used. **1CuP25** shows better photocatalytic activity than **1NiP25**, and the liquid **HMAS-L** leads to the highest H_2 production (1875 $\mu mol.h^{-1}.g^{-1}_{cat}$), which highlights the revalorization of these residues via photoreforming. Focusing on the H_2/CO_2 ratio, the combination of **1CuP25** and **MC** renders the best results. Furthermore, the present study has proved that a photodegradation test (in absence of a photocatalyst) is an indirect evaluation of the reactivity and degradability of a given substrate in photoreforming.

Acknowledgments

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Photothermal conversion of CO_2 to methane utilizing Ru/TiO_2

Kasper Wenderich, Annemarie Huijser, Guido Mul *

PhotoCatalytic Synthesis Group, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, the Netherlands.

Keywords:

The photothermal reduction of CO_2 to value-added products is a fundamentally and practically interesting reaction to create a sustainable chemical process industry. In this work, we show that TiO_2 decorated with small Ru nanoparticles is a very promising photothermal catalyst for the conversion of CO_2 and H_2 to methane (i.e., the Sabatier reaction) under illumination at mildly elevated temperatures. We will first demonstrate that the light-sensitivity towards selective CH_4 production is very apparent at temperatures of 180 – 200 °C, a behavior observed not only under UV/Vis illumination, but also under visible light illumination. To elucidate the underlying mechanisms, we will show (i) DRIFT spectroscopy studies to understand the surface chemistry occurring and (ii) photoluminescence studies to elucidate the role of charge carriers under UV illumination (267 nm, photoexciting predominantly the TiO_2 support) or visible light illumination (532 nm, photoexciting predominantly the Ru nanoparticles). Through careful analysis of these results, we propose a model for the physical and chemical nature of photothermal CO_2 reduction occurring on the Ru/TiO_2 particles.

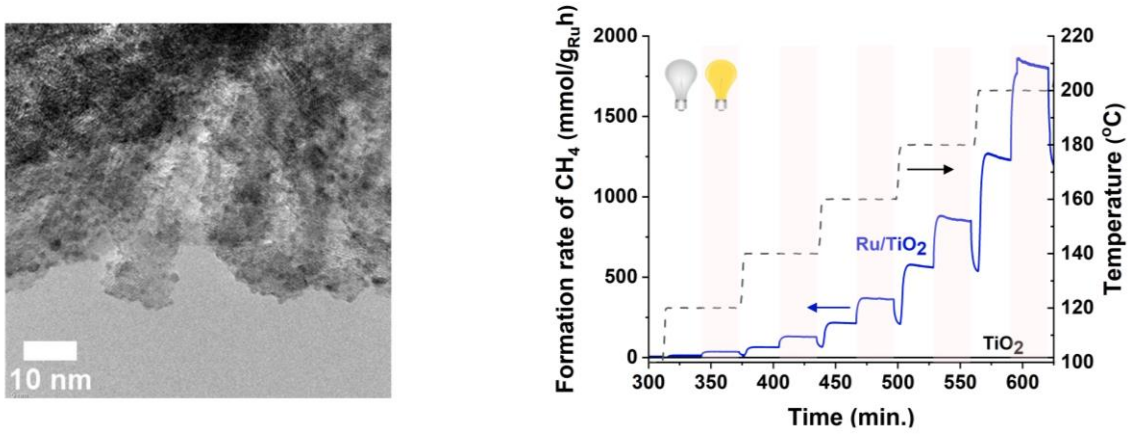

Figure 1. (a) TEM micrograph of the Ru particles attached to the TiO_2 support. (b) Formation rate of methane at various temperature intervals in the absence or presence of radiation. Without Ru, TiO_2 does not show photothermal activity. Please note the strong rate increase upon illumination at 180 and 200

Dual photoredox catalysis toward alkoxy radicals

A. Ondrejková[1*], R. Lindroth[1], G. Hilmersson[1] and C. J. Wallentin[1]

[1]*Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden*
[*]*alica.ondrejkova@chem.gu.se*

Keywords: alkoxy radical, photocatalysis, dual catalysis, chemoselective transformation

Introduction. Alkoxy radicals are species with significant potential in organic synthesis.[1] However, factors such as harsh conditions required for their generation and their highly reactive nature represent a major challenge for their application in a synthetic context.[1] The field of photoredox catalysis allows to access and utilize these reactive species in a controlled manner and simultaneously circumventing harsh reaction conditions.[2 - 4] Regardless, the development of reliable methods for harnessing and utilizing the reactivity of alkoxy radicals remains of great interest to the synthetic community.

Methodology. In this work, we present the photocatalytic method which allows for alkoxy radical-mediated oxidative C(sp^3)-H bond functionalization in a structurally divergent fashion. The presented method employs photoredox/iron dual catalysis to facilitate the chemoselectivity of the transformation. This strategy gives access to two structurally distinct sets of products, tetrahydrofurans and γ-bromoketones, under one set of reaction conditions.

Results and discussion. Chemoselectivity control is achieved by modulating the presence of a metallic needle. In this context, the needle serves as an unprecedented earth-abundant metal catalyst source, which operates in synergy with photoredox conditions. With this photo-driven method in hand, we are able not only to generate alkoxy radicals under mild reaction conditions but also to utilize them in a chemoselectively controlled fashion for an elegant conversion of simple alcohols to two synthetically relevant synthons.

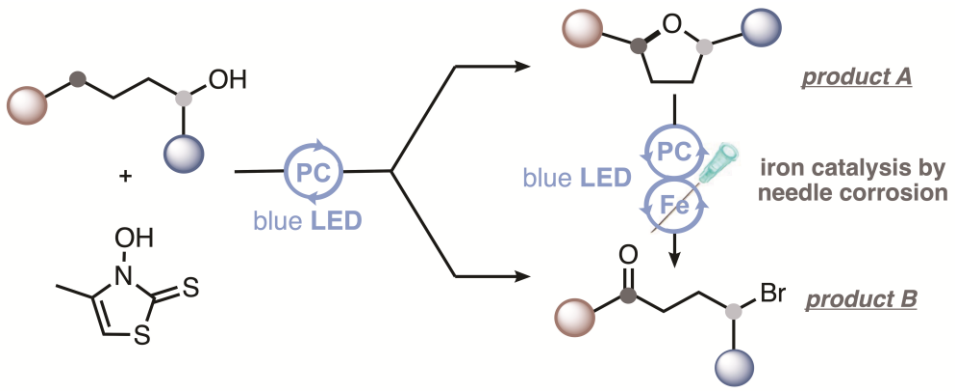

Figure 1. Visible-light mediated oxidative transformation of alcohols to tetrahydrofurans (product A) and γ-bromoketones (product B) employing a dual catalysis approach

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Direct Photocatalytic Synthesis of Acetic Acid from Methane and CO at Ambient Temperature Using Water as Oxidant

Chunyang Dong[1], Maya Marinova[2], Olga Safonova[3], Massimo Corda[1], Yong Zhou[1], Andrei Y. Khodakov[1*], Vitaly Ordomsky[1*]

[1]*Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 – UCCS, F-59000, Lille, France*

[2]*Univ. Lille, CNRS, INRAE, Centrale Lille, Univ. Artois, FR 2638 – IMEC, F-59000, Lille, France*

[3]*Paul Scherrer Institute, CH-5232 Villigen, Switzerland*

[*]*Andrei.Khodakov@univ-lille.fr, Vitaly.Ordomsky@univ-lille.fr*

Keywords: methane, photocatalysis, acetic acid, water

Introduction. Methane is one of the most abundant energy reserve feedstocks on earth, and its direct catalytic functionalization to value-added chemicals holds great interest to the modern scientific community. The current industrial route for methane transformation to obtain acetic acid (AcOH) as an important industrial chemical is an energy-intensive and indirect multistep route through methane reforming to syngas (CO and H_2), methanol synthesis, and subsequent methanol carbonylation to AcOH. The direct routes use strong oxidants such as corrosive acid or molecular oxygen leading to environmental issues, safety risks, and low selectivity[1]. Consequently, realizing a milder oxidative transformation of methane to produce acetic acid would be of great significance.

Experimental/methodology. The catalyst synthesis was realized by stepwise precipitating Pt-anchored ammonium phosphotungstic polyoxometalate (i.e.,$(NH_4)_xPW_{12}O_{40}$, abbreviated as NPW) particles and mixing them with TiO_2 via grinding and heat treatment. The photocatalytic CH_4 conversion was performed in a 100 mL batch photoreactor under 1 bar of CO and 10 bar of CH_4, with a 400 W Hg−Xe lamp used as a light source. Throughout the reaction, the catalyst−water suspension (10 mL) was magnetically stirred at 20 °C.

Results and discussion. Herein, we show that under the irradiation of UV light, CH_4 and CO can be catalytically converted to acetic acid, with H_2O as the sole oxidant at room temperature according to the equation: $CH_4 + CO + H_2O \rightarrow CH_3COOH + H_2$[2]. The characterization shows that the catalyst is composed of isolated Pt atoms anchored by polyoxometalate clusters to TiO_2 (**Figure**). $Pt_1/NPW/TiO_2$ enables a stable synthesis of 5.7 mmol·L^{-1} acetic acid solution in 60 h with the selectivity over 90% and 66% to acetic acid on liquid-phase and carbon basis, respectively, with the production of 99 mol of acetic acid per mol of Pt. Combined isotopic and in situ spectroscopy (XAS, FTIR, EPR) investigation suggests that the C-H activation of CH_4 and subsequent carbonylation occurs at the Pt_1 sites, facilitated by the photo-generated holes from TiO_2 producing ·OH radicals from water; in the meantime, with the assistance of photo-generated electrons, the underlying polyoxometalate cluster served as a reactive oxygen reservoir, realized the oxidation of methyl carbonyl intermediate with subsequent regeneration by water (**Figure**).

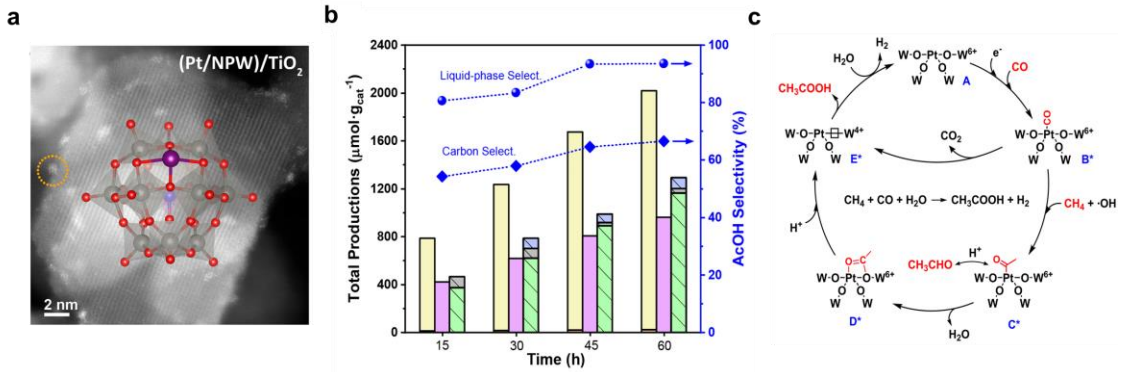

Figure. (a) Atomic-resolved HAADF-STEM image of $Pt/NPW/TiO_2$, (b) accumulated products and selectivity to AcOH, (c) scheme of the reaction.

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Photocatalytic Water Splitting Over Reduced TiO_2

Pınar Özdemir[1], Ramazan Yıldırım[1*]

[1]*Boğaziçi University, Istanbul, Turkey*
[*]*Corresponding Author's E-mail: yildirra@boun.edu.tr*

Keywords: Photocatalytic Glycerol Reforming, Hydrogen Production, Black TiO_2, Reduced TiO_2, Au/B-TiO_2

Introduction. Solar energy, as the largest source in earth, can be used directly or utilized to produce solar fuels such as the hydrogen produced from water via photocatalytic or photoelectrochemical processes. TiO_2 is the most widely used semiconductor in photocatalytic reactions as an abundant, inexpensive and relatively harmless material for human health and environment; however, it needs to be modified (like surface reduction) because its activity is low under visible light [1]. The aim of this study is to investigate the photocatalytic H_2 evaluation of reduced (black) TiO_2 (B-TiO_2), which is known to be more active under visible light, with 1 wt.% platinum (Pt), 0.2 wt.% gold (Au) and 1 wt.% copper (Cu) co-catalysts.

Experimental/methodology. B-TiO_2 was prepared by chemical reduction method with $NaBH_4$ [2]. Whereas Au and Cu were loaded on B-TiO_2 by deposition precipitation with urea [3], Pt was loaded using the incipient to wetness impregnation method. The H_2 production performance of all prepared catalysts were carried out in a semi-batch photoreactor system, equipped with a solar simulator having 300 W xenon lamp, at ambient condition using 1.0 gcat/L in 20 wt.% aqueous methanol (MeOH) or glycerol (GLY) mixtures under argon atmosphere. The determination of H_2 production rate was carried out via a gas chromatograph system.

Results and discussion. The photocatalytic H_2 evolution performance of Pt, Au, and Cu supported on reduced nano TiO_2 was tested in MeOH and GLY aqueous mixtures under visible light (Fig. 1a). The hydrogen production was much higher with GLY solution while Au was the best performing co-catalyst with GLY even though its loading was 1/5 of Pt. The characterization tests revealed that the reduction of nano TiO_2 with $NaBH_4$ was successful as evident from the change of color from white to black and TEM analysis that shows ~1.5 nanometer of disordered layer on the surface (Fig. 1b-d). Decreased band gap and higher light adsorption (Fig. 1e-f) in visible region indicates the visible light sensitivity of B-TiO_2 by reduction. Au was well dispersed on the surface as spherical particles as expected from the deposition precipitation method (Fig. 1g-h), and desirable to see the plasmonic effects under visible light.

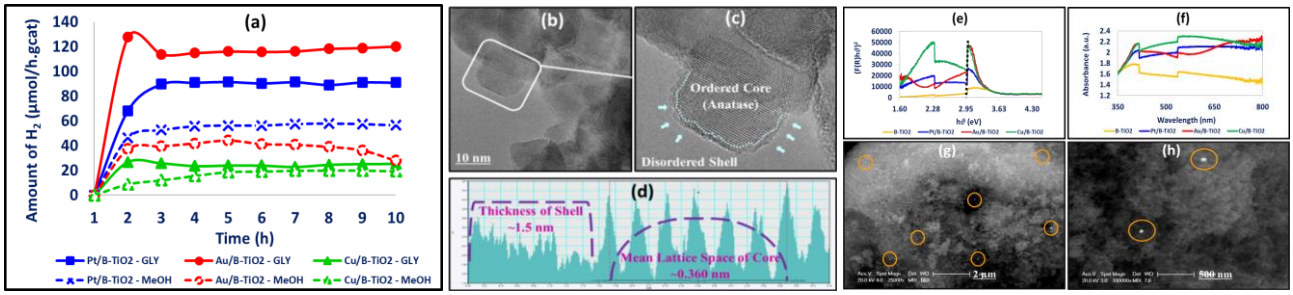

Fig. 1. (a) The H_2 evolution performance of B-TiO_2 based catalysts in MeOH and GLY aqueous mixture under visible light, **(b,c and d)** TEM images and lattice space of B-TiO_2, **(e-f)** UV-Vis absorption spectra and bandgap energy of B-TiO_2 based samples, **(g-h)** SEM images of 0.2 wt.% Au over support, respectively.

Acknowledgments
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An Optofluidic Planar Microreactor for Photocatalytic Water Splitting Reaction under Visible Light illumination

Laxmi Prasad Rao Pala[1], Nageswara Rao Peela 2*

[1]*Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam, 781039, India*
[2]*Department of Chemical Engineering & Center for Nanotechnology, Indian Institute of Technology Guwahati, Assam, 781039, India*
[*]*peelanr@iitg.ac.in*

Keywords
Optofluidic planar microreactor, Iridium oxide, Titanium dioxide thin film, Photocatalytic water splitting, Oxygen evolution; Sol-gel spin coating

Introduction

Since the discovery of photoelectrochemical cell (PEC) using TiO_2 material for water splitting to produce H_2 and O_2 by Fujishima and Honda, the semiconductor photocatalysis has been receiving considerable attention[1]. Powder suspensions are usually implemented to study the photocatalytic water splitting activity. Although the reactor system (e.g., slurry reactor) is simple, it has drawbacks such as lower light penetration because of solution turbidity, lower utilization of active catalytic sites, lower surface area to volume ratio and separation of catalyst material after reaction. These problems can be alleviated by employing immobilized photocatalyst based optofluidic microreactors[2]. Such microreactors can provide high surface area to volume ratio and thus excellent mass and photon transfer efficiency. Among various optofluidic microreactors, the planar microreactor has advantages of higher photon receiving area, throughput and easy scale-up[3]. Therefore, the objective of the present work was to fabricate the optofluidic planar microreactors with the immobilized TiO_2-based photocatalyst and to use it for the production of green hydrogen and oxygen from the photocatalytic water splitting under visible light by the deposition of Pt and IrO_2, respectively.

Experimental/methodology

Optofluidic planar microreactor for production of oxygen[4,5,6]:

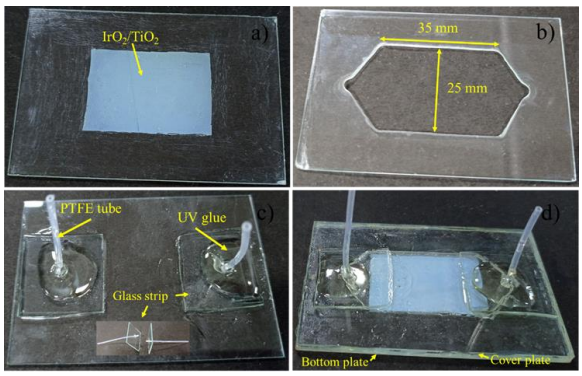

Figure 1. a) Bottom plate with catalyst coating; b) Reaction chamber; c) Cover plate with inlet and outlet tubes; d) Fabricated planar microreactor. (Reproduced from Ref. 6 with permission)

Results and discussion

The effect of reactant flowrate on the rates of hydrogen (HER) and oxygen (OER) production is shown in Fig. 2. In both the cases, the production rate was increased initially (at lower flowrates) and then decreased passing through a maximum at 0.3 mL min^{-1}. The increase in the production rate with increase of flow rate up to 0.3 mL min^{-1} could be due to the presence of the external mass transfer resistance at lower flow rates. Beyond 0.3 mL min^{-1}, the decrease in the production rate could be due to the decrease in the

reactant residence times. Therefore, 0.3 mL min^{-1} was found to be an optimal reactant flowrate where the maximum production rates of both HER and OER were obtained.

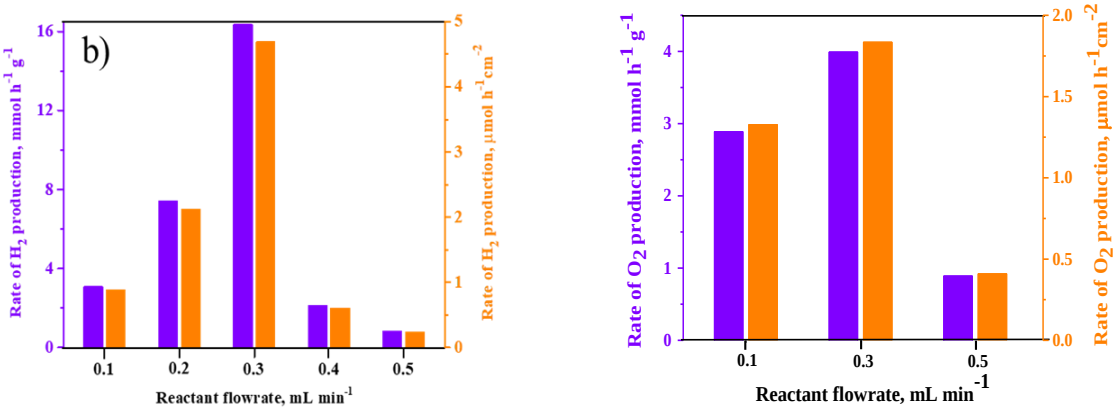

Figure 2. (a) Rate of hydrogen production (Reaction conditions: Reactant-20 vol.% methanol in DI water, Pt/TiO_2 film); (b) Rate of oxygen production (Reaction conditions: Reactant-10 mM $NaIO_3$ in DI water, IrO_2/TiO_2 film); as a function of reactant flowrate. (Reproduced from Ref.s 5 and 6 with permission)

Conclusions

The optofluidic planar microreactors were fabricated and tested successfully for the photocatalytic water splitting for the production of both hydrogen and oxygen, under visible light. The rates of hydrogen and oxygen production were passed through a maximum with reactant flowrate. The hydrogen and oxygen production rates of 16.35 mmol h^{-1} g^{-1} (4.7 µmol h^{-1} cm^{-2}) and 4.0 mmol h^{-1} g^{-1} (1.84 µmol h^{-1} cm^{-2}) were obtained over the Pt/TiO_2 and IrO_2/TiO_2 films, respectively, at an optimum reactant flowrate of 0.3 mLmin^{-1}.

Acknowledgments

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Photosensitised PCET mediated β-Scission of alcohols for addition reactions

Y. Patehebieke, H. P. Bryce-Rogers, C. J. Wallentin*

Department of Chemistry and Molecular Biology, University of Gothenburg, 412 96 Gothenburg, Sweden
carl.wallentin@chem.gu.se

Introduction. With recent advances in photocatalysis and radical chemistry, radical-mediated C-C bond cleavage has emerged as a powerful disconnection strategy for the rapid assembly of structurally diverse carbon skeletons. Among them the alkoxy radical mediated deconstruction and functionalization have attracted considerable research attention. As a highly reactive transitory species alkoxy radicals have a well-known variety of reactivity, such as hydrogen atom transfer, addition to π systems,and β-scission. The homolytic cleavage of an adjacent β-C-C bond provids C-centred radicals, such species can further be used in a variety of both intra- and intermolecular transformations. [1]

Due to the high bond dissociation energy (BDE ~105 kcal mol^{-1}) and redox potential of alcohol O–H bond the direct formation of an alkoxy radical from a free alcohol is formidably challenging. Hence, most common methods rely on O-functionalized precursors to generate alkoxy radicals. Employing prefunctionalised alcohol-auxiliary precursors that undergo thermal/photo/radical induced homolysis, has the drawbacks of tedious synthetic prefunctionalisation, poor stability, toxicity, and narrow functional group tolerance. [2]

Recent development in transitionmetal and photoredox catalysis have enabled direct access to alkoxy radicals from unprotected alcohols. However, many of these methods require the use of precious metalcatalysts or stoichiometric oxidants. [2] As such, the developing more sustainable approaches for the generation of alkoxy radicals directly from alcohols is an important and timely pursuit.

Here we present a novel photocatalytic method for one carbon-tethering of nucleophiles and electrophiles via β-scission of alkoxy radicals which directly generated from secondary and tertiary alcohols.

Results and discussion. In this work, a successful study utilising an indirect proton-coupled electron transfer (PCET) mediated procedure, showcasing the formation of a diverse library of C-sp^3 radical nucleophiles. Subsequently, these radical intermediates are synthetically utilised to build molecular complexity onto a range of coupling partners. The protocol allows for the efficient intermolecular tethering of a nucleophile and an electrophile via a methylene group.

Acknowledgments
We gratefully acknowledge the Knut and Alice Wallenberg Foundation for financial support.

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Photo-assisted H_2 production and hydrogenation reactions

Yong Peng,[1] Josep Albero,[2] Henrik Junge,[3] Hermenegildo Garcia,[4]* Matthias Beller[5]*
[1,3,5]*Leibniz-Institut für Katalyse e. V., Rostock, Germany*
[2,4] *UPV Instituto de Tecnología Química, Valencia, Spain*
[*]*hgarcia@qim.upv.es; Matthias.Beller@catalysis.de*

Keywords: Photocatalysis, Formic acid, Hydrogen production, CO_2 hydrogenation, N_2 hydrogenation.

Introduction.

Tranditionally, H_2 releasese from formic acid needs the input of external energy to reach a high temperature for a decent activity, especially when heterogenous catalyst is applied. The aim of this research is to explore the production of H_2 from formic acid with the assistance of light, eliminating or minimizing the need for external energy input. Additionally, we aim to utilize the released H_2 for cascade hydrogenation reactions. However, many hydrogenation reactions, such as CO_2, CO, and N_2 hydrogenation, typically require high temperatures. Recent advancements have shown that solar energy can promote reactions through photothermal processes. Plasmonic metal nanoparticles (NPs) can absorb incident solar light and induce high localized temperatures. This localized surface plasmonic effect allows most metal NPs to respond to visible to near-infrared light, which matches the solar spectrum, maximizing the utilization of solar energy. Therefore, another objective of this research is to achieve hydrogenation reactions under milder conditions with minimal fossil fuel energy input.

Experimental/methodology.

The formic acid reaction was tested in a semi-batch system connected to a burette, allowing the measurement of produced H_2, as well to maintain ambient pressure. The incident light can be introdued through the top of the photo reactor.

The hydrogenation reactions were performed in a customized fixed bed reaction, in which the incident light can introducd from the top (more detailed information of the reaction can be see in ref. 1).

Results and discussion

(1) We have proved that the formic acid dehydrogenation can be realized upon light irradiation with the absence of external heating, reaching an activity comparable with state of the art activity reported in thermal fashion.
(2) Efficient photocatalysts were obtained for the CO_2 and nitrogen hydrogenation. Specifically, earth abundant hydroxylapatite based catalyst was synthesized, and it exhibited high selectivity towards CO production. For nitrogen hydrogenation, Cs promoted Ru catalyst supported on $SrTiO_3$ or ZrO_2 were synthesis, and both catalysts exhibited high acitvity towards ammonia production.
(3) We have established an efficient photo-assisted hydrogenation reaction setup, and demonstrated that the activity for both CO_2 and N_2 hydrogenation can be efficiently enhanced upon light irradiation.
(4) The role of incident light was elaborated by plenty of experimental results. Specifically, the thermal and nonthermal contribution to the activity were carefully studied.

Acknowledgments

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Photocatalytic selective oxidative cleavage of β-O-4 linkages of a lignin based model compounds by Novel TiO_2 nanomaterials

Abdul Qayyum*, Dimitrios A. Giannakoudakis, Darius Lomot, Juan Carlos Colmenares*
Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
aqayyum@ichf.edu.pl, jcarloscolmenares@ichf.edu.pl

Introduction: Heterogeneous photocatalysis using metal oxide semiconductors is one of the most promising method to achieve the high value aromatic compounds via the cleavage of the inter-unit linkages/bridges of lignin [1]. Titania based nanocatalysts are considered a promising candidate for heterogeneous catalysis due to specific unique physicochemical properties [2]. The reported TiO_2 samples possessed less selectivity toward the products. The key goal of this research work was to synthesize the novel US-assisted TiO_2 nanomaterials for the significantly higher photocatalytic selective cleavage of β-O-4 bond of a lignin based model compounds to the corresponding products.

Experimental: In this research work, low-frequency ultrasound (US) 22 kHz with varying the amplitudes (such as 10, 30, 50, 70 and 90 µm) was used during the precipitated synthesis of TiO_2 catalysts. The synthesized TiO_2 catalysts were characterized with different characterization techniques such as XRD, UVDRS, TEM, XPS and TGA. All the synthesized TiO_2 samples were studied for the catalytic selective cleavage of lignin based model compounds such as benzyl alcohol and 2- phenoxy-1-phenylethanol (PP-ol) to the corresponding products **(Figure 1a)** under the UV (365 nm) light irradiation.

Results and discussion: The US-assisted TiO_2 sample by using 30 µm showed the highest specific surface area (319 m^2/g) and total pore volume (0.339 cm^3/g) as compared to all other synthesized samples. Electron microscopy analysis showed the utilization of US during step led to the formation of nanorods. The photocatalytic performance of all the US assisted TiO_2 samples was pre-screened by evaluating the partial selective oxidation of benzyl alcohol to benzyl aldehyde. The US22-30µm catalyst showed the highest conversion of benzyl alcohol (75%), and yield of benzyl aldehyde (68 %) as compared to all other US assisted synthesized TiO_2 catalysts.

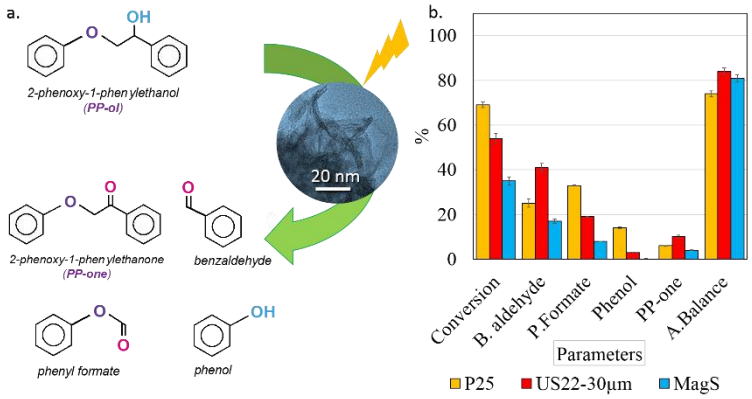

Figure 1. The schematic of the targeted reaction (a), photocatalytic activity of TiO_2 samples (b)

P25 showed the highest conversion (67 %) of PP-ol with the 25 % yield of the benzyl aldehyde, which is the desired product, whereas as US22-30µm showed lower conversion (56%) of PP-ol but a higher yield (45%) of benzyl aldehyde **(Figure 1b)**. Whereas, the MagS showed the least PP-ol conversion of 34 %. This research work showed that optimizing not only the frequency but also the amplitude of the sonication play a key role on the synthesis of metal oxide-based catalysts and the physicochemical features as well as the photocatalytic performance of synthesized catalysts can be tuned accordingly.

Acknowledgments:
National Science Centre in Poland: OPUS-13 project nr 2017/25/B/ST8/01592 and http://photo-catalysis.org

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Harvesting plasmonic effects for H_2 evolution and CO_2 reduction reactions

F. Rathmann[1*], I. Abdelsalam[2‡], A. L. Reznichenko[3], M. Reinikainen[4], P. H. C. Camargo[5]

[1,3,4]*VTT Technical Research Centre of Finland Ltd, Espoo, Finland*
[2,5]*University of Helsinki, Helsinki, Finland*
[*]*Florian.Rathmann@VTT.fi*, [‡]*Ibrahim.Abdelsalam@Helsinki.fi*

Keywords: Plasmonic catalysis, nanorattles, visible light, CO_2 reduction

Introduction.

Plasmonic nanorattles (PNRs) have gained attention due to their unique and enhanced optical properties compared to spherical nanoparticles. Their structure consists of a core inside a shell which are separated by a void between them. This results in the hybridization of localized surface plasmon resonance modes between the core and shell leading to the formation of electromagnetic hot-spots, that can contribute to improved performances in plasmonic catalysis relative to spherical nanoparticles.[1] Additionally, the porous shell can be comprised of a combination between a plasmonic and catalytic component, providing a unique antenna-reactor design.[1,2] In this poster, we will present recent advances on the development of PNRs consisting of an Au core, surrounded by an alloy shell of Ag and Pt or Pt, respectively, as a plasmonic catalyst towards the H_2 evolution reaction (HER) and CO_2 reduction reactions.

Experimental/methodology.

The PNRs were fabricated by a solution-phase approach consisting of a three-step process. The first step involved the preparation of Au NPs by the Turkevich method. In the second step, an Ag shell is formed by a seeded-growth process, whereby ascorbic acid is used as reducing agent in both steps. The third step involved the galvanic replacement of Ag with Pt or Pd by using PVP as a capping agent.[1] The particles were characterized by elemental analysis, electron microscopy, and using UV-Visible absorption spectroscopy. For HER studies linear sweep voltammetry (LSV) measurements are performed in 0.5 M H_2SO_4 with a scanning potential range from 0.1 to -0.3 V (vs. RHE). To prepare the electrodes, an ink consisting of a mixture of the sample and vulcan carbon in a Nafion solution is drop-casted onto a glassy carbon electrode. The CO_2 reduction reactions are investigated in a fixed bed reactor under different parameters, such as temperature, pressure, and light excitation of the PNRs. The reduction products are measured by a GC-MS.

Results and discussion.

We focused so far in PNRs containing Au as a core and two types of plasmonic-catalytic shells: AgPd or AgPt, leading to Au@AgPd and Au@AgPt PNRs, respectively. Our data shows that our procedures were effective for the synthesis of the PNRs with the desired morphological and compositional features, presenting LSPR bands in the visible range. In terms of the activity towards the HER, our initial catalytic data with the Au@AgPd PNRs suggest a reduction in the overpotential under visible light illumination. Regarding the CO_2 reduction reaction, the performances and the establishment of structure-performance relationships are under investigation. To this end, the PNRs synthesis has been scaled-up and the PNRs have been deposited into commercial SiO_2 as supports by dry impregnation. A detailed investigation of catalytic performances as a function of the PNRs compositions, morphological features, light excitation wavelength and intensity, as well as the benchmarking of performances relative to dark conditions and conventional NPs catalysts or plasmonic materials are under investigation.

Conclusion.

In this work, PNRs have been prepared by a combination of seeded growth and galvanic replacement approaches. These PNRs are being employed as plasmonic catalysts towards both the HER from water and the CO_2 reduction. Initial catalytic data indicate that visible light excitation leads to an activity enhancement. We aim to combine advanced optical and morphological characterization with results from the catalytic tests to unravel structure-performance relationships and enhancement mechanisms under light excitation.

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Photoelectroreduction of nitrates to ammonia in hybrid plasmonic nanocatalysts

Vitor R. Silveira [1], Robert Bericat-Vadell [1], Jacinto Sá [1 *]

[1] *Physical Chemistry Division, Department of Chemistry - Angstrom Laboratory, Uppsala University, Box 523, 751 20 Uppsala, Sweden*

[*] *jacinto.sa@kemi.uu.se*

Introduction. Advancements in farming practices have resulted in the widespread use of nitrogen-based fertilizers, such as ammonia, produced by the nitrogen reduction in the Haber-Bosch process. [1] Extensive efforts have been made to create alternative, eco-friendly methods for ammonia production on a large scale that can be implemented locally. In that sense, the reduction of nitrates (NO_3^-) present as a potential method to substitute the nitrogen reduction reaction. [2] We suggest a NiO/Au/TiO_2 photosystem that selectively creates ammonia from nitrates using visible light at normal pH and temperature through plasmon hot electrons.

Experimental/methodology. The catalyst's thin films were synthesized over a conductive glass (FTO) by a combination of screen printed NiO (Solaronix®), spray coated Au NPs (8 nm, synthesized by Turkevich method), and spin coated TiO_2 (Solaronix®). These catalysts were then characterized with steady-state and transient spectroscopy. Electrocatalytical studies were conducted in a gas-tight single compartment cell, using Ag/AgCl reference electrode and Pt wire counter electrode in KNO_3 0.2 M aqueous solution. The cell worked under continuously flow of Ar (30 mL min^{-1}) and its outlet was connected to a quadrupole mass spectrometer, which measured online the gas produced during the reaction. In the end of the reaction, NH_4^+/NH_3 and NO_2^- production were quantified through photometric methods.

Results and discussion. Figure 1 depicts the generation of ammonia and nitrite using the full photocatalyst (NiO-Au-TiO_2) and its counterparts. It is noteworthy to observe that all systems exhibit the formation of NO_2^-, indicating that this species acts as an intermediary in the reaction, aligning with previously documented mechanisms of nitrate hydrogenation. [2] Furthermore, the results suggest that TiO_2 presents high selectivity towards ammonia production, even in the absence of light, due to its ability to effectively bind both NO_3^- and the intermediate NO_2^-. On the other hand, the other catalysts generate NO_2^- which is then released into the solution, thereby cleaning the active sites, resulting in greater conversion of NO_3^- to NO_2^-. This leads to the interesting conclusion that the active site for NO_3^- reduction is the same to that of NO_2^- reduction. With regards to the impact of photogenerated carriers on the catalytic activity, the results demonstrate that NiO-Au-TiO_2 exhibits the most pronounced difference in the formation of ammonia and nitrite ions between illuminated and dark conditions, compared to other TiO_2-based counterparts. This trend is in accordance with the higher charge separation facilitated by the presence of a hole and electron acceptor in NiO-Au-TiO_2, as indicated by the transient spectroscopy measurements not reported in this abstract. Online measurement of generated gases revealed limited hydrogen gas production (a common competitor in nitrate reduction) at lower potentials and suppressed hydrogen production under light conditions at higher potentials. This indicates improved charge separation in the hybrid plasmonic nanocatalyst results in increased ammonia formation and decreased hydrogen production.

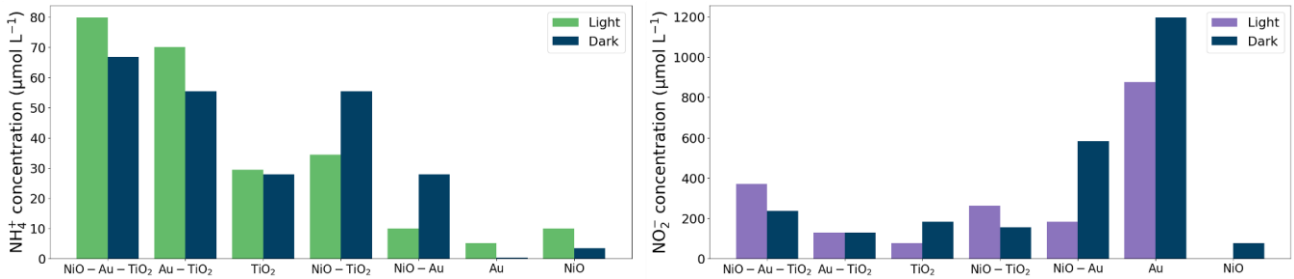

Figure 1. Formation of ammonium (left) and nitrite ions (right) at -1.21 V vs Ag/AgCl in KNO_3 0.2 mol L^{-1} over a thirty-minute interval under both illuminated and dark conditions.

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Photocatalytic CO_2 Conversion on Edge-truncated Cubic Cu_2O Crystal with Controlled Photogenrated Charge Carrier Dynamics

Aloka Kumar Sahu[1, 2*], Meenakshi Pokhriyal[1], Xiu Song Zhao[2*], Sreedevi Upadhyayula[1*]

[1]*Indian Institute of Technology Delhi, Hauz Kash, New Delhi 110016, India*
[2]*The University of Queensland, Brisbane, QLD 4072, Australia Brisbane, Australia*
[*]*george.zhao@uq.edu.au; sreedevi@chemical.iitd.ac.in*

Keywords: photocatalyst, photogenerated charge carriers, CO_2 conversion

Introduction: Photocatalytic conversion of CO_2 and water into fuel and commodity chemicals offers a potential green route towards a circular economy but is challenging due to the multi-proton-electron transfer steps involved and sluggish surface reaction kinetics.[1,2] Effective separation, migration, and capture of photogenerated charge carriers are key parameters to enhance the CO_2 conversion efficacy of photocatalysts.[3] Here, through computational simulations of Cu_2O crystals with different facets, edge-truncated cubic Cu_2O crystal was confirmed to enable efficient charge separation and experimental results revealed that the promotion of photocatalytic CO_2 reduction reaction and water oxidation reaction on the reduction {110} and oxidation {100} facets, respectively.

Experimental/methodology: Using standard precipitation and reduction techniques, two distinct Cu_2O photocatalyst morphologies were synthesized, one with cubic crystals and the other with edge-truncated cubic crystals. The steady-state photoreduction reactions were carried out using a 300 W Xe lamp light source with AM 1.5 G filter. The morphologies and structures of photocatalysts were determined by transmission electron microscopy. The crystallinity and elemental compositions of photocatalysts were measured by powder X-rat diffraction patterns energy-dispersive X-ray photoelectron spectroscopy analysis. The photoresponse data were obtained through UV-vis spectra and photoluminescence spectroscopy.

Results and discussion: The photocatalytic activity toward the selective reduction of CO_2 to methanol on the edge-truncated cubic Cu_2O with anisotropic {100} and {110} facets was found to be nearly 5.5-fold higher than that of cubic Cu_2O with only {100} facets (**Figure 1a**) and were also stable for multiple photocatalytic cycles (**Figure 1b**). This observed difference is ascribed to the effective separation and migration of photogenerated charge carriers as well as the selective accumulation of electrons and holes on different facets of edge-truncated cubic Cu_2O crystals (**Figure 1c**), which was confirmed through the optoelectronic simulations of modeled edge-truncated Cu_2O crystal.

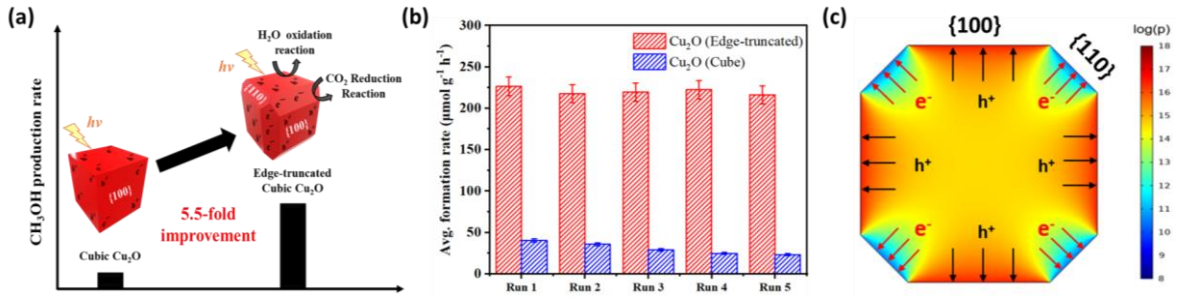

Figure 1: (a) Photocatalytic CO_2 reduction performances of prepared samples in atmospheric conditions. (b) Stability test of both photocatalysts after five cycles. (c) A simulated 2D-surface plot of edge-truncated Cu_2O crystal.

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Characterization and evaluation of photolabile cage substrates towards enabling time-resolved diffraction-based studies of *ba*$_3$-type cytochrome *c* oxidase

Emil Sandelin[a], Jonatan Johannesson[a], Ola Wendt[b], Gisela Brändén[a], Richard Neutze[a] and Carl-Johan Wallentin*[a]

[a] *Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden.*
[b] *Centre for Analysis and Synthesis, Department of Chemistry, Lund University, Lund, Sweden.*
Email: *carl.wallentin@chem.gu.se

Introduction. Arguably, few other methods have led to the type of scientific revolution as revealing the structure-function relationship between proteins and the mechanism of life and has been a staple of structural biology ever since. Technological advances in X-ray generation at synchrotrons and more recently X-ray free electron lasers (XFEL:S) has provided access to brilliant, short X-ray pulses which in conjunction with traditional pump-probe techniques have laid the foundation for time resolved (TR) diffraction-based experiments.[1] The scope of available proteins has been restricted to photo responsive proteins and to expand the scope of targets, new tools must be developed. The use of photolabile cage substrates has recently become a discussed topic within structural biology[2] and in our work we have employed (μ-peroxo)-(μ-hydroxo)bis[bis(bipyridyl)cobalt (HPBC) caged-oxygen complexes which can liberate millimolar concentrations of molecular oxygen upon a single laser pulse to study *ba*$_3$-type cytochrome c oxidase with the use of synchrotron and XFEL based diffraction studies.

Results and discussion. In this work we have synthesized and characterized several new caged oxygen compounds (Figure 1) and developed a protocol to enable reaction initiation between reduced microcrystals of *ba*$_3$-type cytochrome c oxidase and molecular oxygen liberated by a caged oxygen complex under conditions to enable further diffraction-based studies. With the developed protocol in hand, we were able to record room-temperature serial femtosecond crystallography (SFX) data of *ba*$_3$-type cytochrome c oxidase 10 ms after oxygen liberation with a 355 nm laser pulse which shows structural rearrangement of the proteins active site (Figure 2).

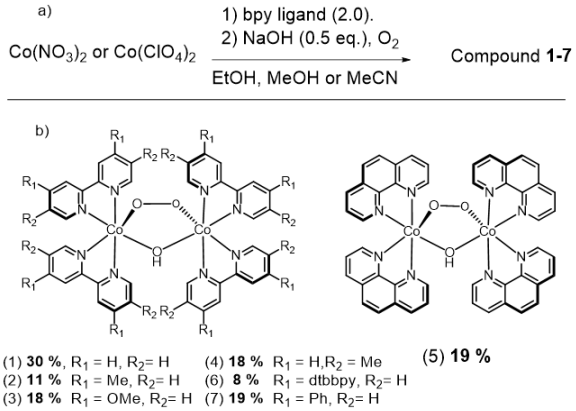

Figure 1. a) Overall reaction scheme for the synthesis of Compound **1**-**7**. **b)** Structure and isolated yields of the produced HPBC complexes.

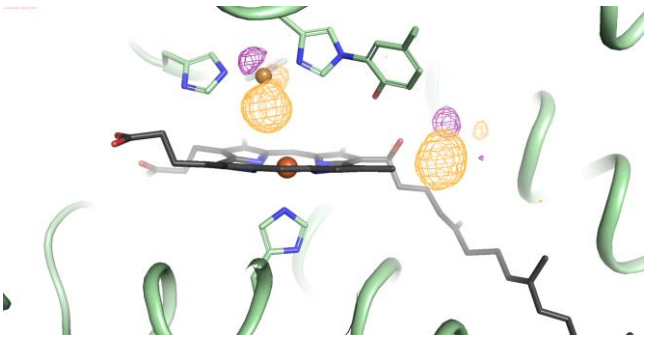

Figure 2. Preliminary F^{obs} - F^{obs} difference Fourier electron density map (yellow negative difference density, purple positive difference density, contoured at ± 5 σ) of *ba*$_3$-type cytochrome c oxidase at t = Δ10 ms after oxygen liberation with a 355 nm laser pulse of compound 1 mixed with microcrystals of reduced protein.

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A fundamental approach to the design and engineering of active photoelectrodes for solar water splitting

Taymaz Tabari[1*], Marcin Kobielusz[1], Wojciech Macyk[1]

Faculty of Chemistry, Jagiellonian University, ul. Gronostajowa 2, 30-387, Kraków, Poland
[*]Corresponding Author's E-mail address: taymaztabari@gmail.com / taymaz.tabari@uj.edu.pl

Keywords: rod architecture, hole consumption, mediator, photoelectrocatalysis

Introduction.

Water splitting is an uphill reaction, which needs 237 kJ to produce one mole of hydrogen. To provide it, solar energy can be used to oxidize/reduce water. Despite the numerous attempts to design efficient photoelectrodes in solar water splitting, the reported efficiency is far from reaching the expected theoretical values. This stems from the intrinsic slow charge transportation, and inefficient charge separation, along with poor oxidation kinetics of the photocatalysts such as TiO_2, Fe_2O_3, etc. Norskov et al. have shown that these photocatalytic systems are unable to efficiently produce oxygen, favoring the production of H_2O_2. This phenomenon points to the importance of employing active oxygen evolution reaction (OER) electrocatalysts to increase the efficiency of water splitting in a PEC system. On the other hand, an efficient charge separation at the bulk is a necessity for a photocatalytic system. In this context, 1D materials due to their directional charge transfer showed promising efficacy in charge separation. Herein, we have used a fundamental approach to design active photoelectrodes for solar water splitting constructed in a heterojunction architecture.

Experimental/methodology. The materials were synthesized employing hydrothermal, and sol-gel methods, while to build the heterojunction architecture a spin-coater was used. The photoelectrodes were studied using XRD, XPS, SEM, TEM, UPS, Kelvin probe, and electrochemical methods. The photoelectrochemical (PEC) activity is studied in a gas-tight reactor with an irradiation widow of 1 cm^2.

Results and discussion. In this collective study, we have shown that the most efficient 1D structure photoelectrodes are constructed from long rods with small diameters, which dramatically decreases charge recombination and increases charge separation. Such rods amounted to 0.24% "applied bias photon to current efficiency", which was among the highest activities reported for pristine and heterojunction TiO_2 [1]. However, the activity of the photoelectrodes correlates with the OER activity of the catalysts employed to oxidize water. In a series of $La_{1-x}Sr_xFeO_3$ (x = 0, 0.2, 0.4), we have shown that the catalytic activity and the overall PEC activity of the photoelectrodes are correlates with the length of Fe–O bond in these perovskites. The overall activity of the photoelectrodes in solar water splitting was a function of the band bending degree and hole consumption at the interface with electrolyte [2]. High solar to hydrogen efficiency can be obtained when both factors are designed to perform efficiently. However, the hole transfer at bulk and specifically at the interface of two semiconductors in a heterojunction design is hindered by the increased oxygen vacancies and decreased conductivity. Therefore, to improve the charge transfer at the bulk and diminish the back charge transfer, reduced graphene oxide is employed as a 2D mediator to direct the holes to the surface of the photoanode, while at the same time preventing back electron transfer. This architecture, constructed from 1D@2D@0D components, showed the highest activity reported for Fe_2O_3-based photoelectrodes, which are related to the optimized electronic and structural properties of it [3].

Acknowledgments

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Methane Oxidative Coupling on Au-TiO_2 Catalyst: DFT Studies

V. Kaipanchery, R. Tokarz-Sobieraj, D. Rutkowska-Zbik*

Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Krakow, Poland
** dorota.rutkowska-zbik@ikifp.edu.pl*

Introduction. Direct conversion of methane into fuels and platform molecules is hampered by its inertness, leading to the necessity of harsh reaction conditions to accelerate its reactivity. In recent years, a combined photo- and thermo-catalytic approach to activate mathane was proposed. Experimental studies show that Au-TiO_2 catalyst under UV/VIS light irradiation is selective in the oxidative coupling of methane to ethane [1]. The aim of the current contribution is to characterize the properties of the Au-TiO_2 catalyst and to study the mechanism of the methane coupling reaction under thermal and photocatalytic conditions.

Experimental/methodology. Quantum-chemical calculations were performed in the frame of Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) with a PBE+D3 and B3LYP+D3 functionals and the def2-TZVP basis set. The geometry and electronic structure of the catalytic system was characterized by computing selected bond lengths, Mayer bond indices, ESP charges on the exposed surface sites, and the DOS plots.

Results and discussion. The system consisting of Au_{13} metallic cluster deposited on TiO_2 was proposed as the model of the active site for the reaction (see Figure 1a) and was characterised with the DFT method. The deposition of the gold cluster resulted in the reduction of the HOMO-LUMO gap of the TiO_2 suppport, facilitating the charge transfer between the metallic cluster and the support. As a result of light absorption, the electron transfer is encountered and formation of the $TiO_2^{\delta+}$ and $Au^{\delta-}$ is observed.

Then, methane interaction with various sites on the Au-TiO_2 catalyst was considered to find the most probable active site for the reaction. The interface between the gold particle and the support or the vacant site at the titanium dioxide are the two preferred sites for the CH_4 adsorption. The C-H bond activation of methane requires 146 kJ/mol when occurring at the $TiO_2^{\delta+}$ phase. This energy, however, is lowered to 67 kJ/mol when occurring at the gold – titania interface (see Figure 1b). During the reaction, gold cluster undergoes significant reorganization. Most probably, the coupling between two methyl groups and formation of ethane takes place at the surface of the catalyst.

a) b)

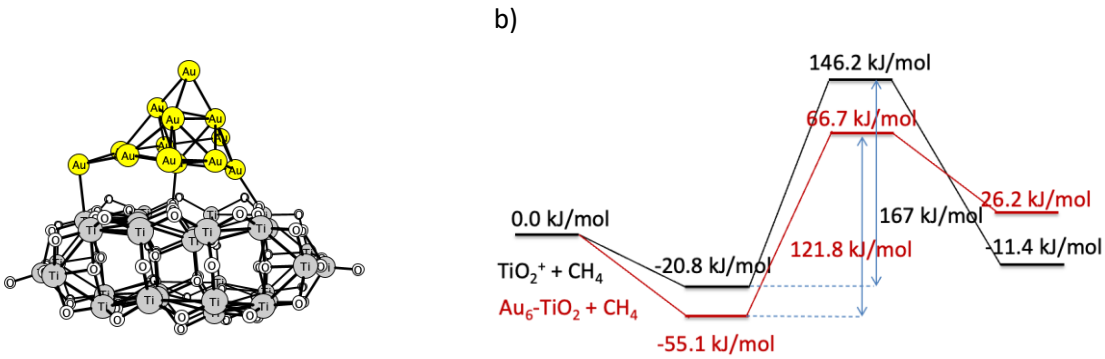

Figure 1: a) model of the Au-TiO_2 catalyst; b) proposed CH_4 activation energy diagram.

Acknowledgments

This work was supported by the National Science Centre, Poland within Solar-Driven Chemistry project no 2019/01/Y/ST4/00024.

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Photo-thermo-catalytic properties of heteropolyacid-TiO_2 systems

A. Micek-Ilnicka[1*], M. Synowiec[2], M. Radecka[2], P. Niemiec[1], R. Tokarz-Sobieraj[1]
[1] *Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Kraków, Poland*
[2] *AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Kraków, Poland*
[*] *anna.micek-ilnicka.ikifp.edu.pl*

Keywords: photocatalyst, heteropolyacid, TiO_2, photo-termo-catalysis, n-butanol dehydration

Introduction. The TiO_2 is widely used as a photocatalyst. This fact motivated us to irradiate the solid heteropolyacid-TiO_2 catalysts by UV light during the gaseous alcohol conversion. The n-butanol conversion was carried out comparatively in both the thermo-catalytic and the photo-themo-catalytic modes as innovative approach (Fig. 1). The application of this reaction has a twofold motivation. First this reaction is of practical relevance, being related to biomass processing, which is a potential source of n-butanol, readily acquired from sugars using Clostridium bacteria. Secondly, the alcohol dehydration over heteropolyacid-TiO_2 (HPA/TiO_2) catalysts uses their acidic protons and thus allows to establish their order of acidity. Moreover our recent research has showed that the catalytic activity of HPA/TiO_2 nanocomposites strongly depends on the used TiO_2 polymorph [1].

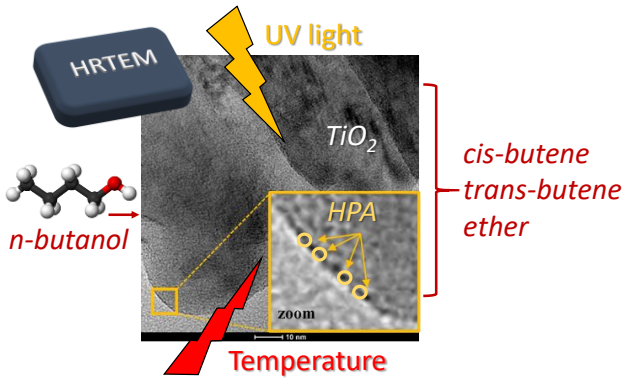

Fig.1. Schematic illustration of reaction

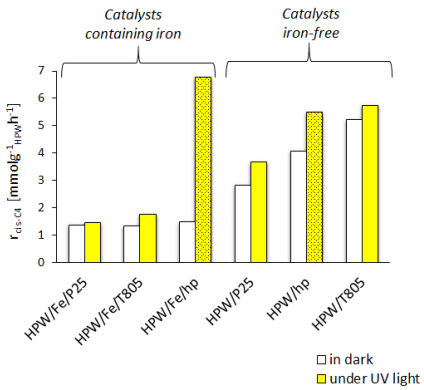

Fig. 2.Rate of cis-C4 formation over solid catalysts upon UV light

Experimental/methodology. As an active phase $H_3PW_{12}O_{40}$ (HPW) heteropolyacid was applied. In turn the photocatalytic oxides: Fe_2O_3 and TiO_2 were tested as the additive and support, respectively. In the case of TiO_2 such as home-prepared (hp) and commercial, hydrophobic T805 and the hydrophilic P25 oxides, with different morphological forms like cubes, nanobars and tiles were applied. Two series of catalysts were synthesised: HPW/TiO_2 and HPW/Fe_2O_3/TiO_2. The authors constructed special photocatalytic chamber with UV light which was connected on-line with GC. Such way allows to monitor this gaseous reaction without or with light. The broad spectrum of techniques such as XRD, HRTEM, UV-vis, FTIR and Raman spectroscopies, XPS, BET analysis and GC were used to characterize the physicochemical (including optical) properties of these photocatalysts. The electronic and geometry structure of heteropolyacid-TiO_2 systems was determined within DFT (PBE+D3/def2-TZVP) and their theoretical spectra simulated within TD-DFT.

Results and discussion. Four main factors to be of critical importance for achieving high catalytic activity of HPA/TiO_2 nanocomposites were identified: type of TiO_2 polymorphs, their surface area, hydrophobic properties, and acid strength [2]. The best performance was observed for HPW/Fe_2O_3/hp and HPW/T805 catalysts. The last one is active most likely as a result of hydrophobic nature of T805 support, that protects the proton sites from competing effect of H_2O molecules with respect to alcohol molecules. The iron addition into HPA/Fe_2O_3/TiO_2 nanostructures caused the increase of selectivity to di-n-butyl ether. The UV light use is mainly manifested by significant increase of cis-butene rate formation (Fig. 2).

Acknowledgments *A part of this work was supported by the National Science Centre, Poland within Solar-Driven Chemistry project no 2019/01/Y/ST4/00024.*

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Improvement of Photoelectrocatalytic Activity and Stability of WO_3 for Oxygen Evolution by Loading Brownmillerite Ca_2FeCoO_5 as a Cocatalyst

E. Tsuji, Y. Degami, H. Okada, S. Suganuma and N. Katada

Center for Research on Green Sustainable Chemistry, Tottori University, Tottori, Japan
e-tsuji@tottori-u.ac.jp

Keywords: cocatalyst, WO_3, water splitting

Introduction. The increasing demand of hydrogen as a clean energy resource and a chemical feed stock has promoted the development of photocatalysts for water splitting. WO_3 is one of the most promising photocatalysts acted under visible light illumination. However, there are mainly two problems; (i) oxygen evolution reaction (OER) on WO_3 is kinetically slow, and (ii) peroxide species is also formed during photooxidation of water, inducing rapidly photocorrosion of WO_3. One of the effective strategies to improve OER activity and stability of WO_3 is loading of OER cocatalysts. In this study, we report improvement of photoelectrocatalytic activity and stability of WO_3 for OER by loading brownmillerite-type Ca_2FeCoO_5 (CFCO) [1], which showed higher OER activity than noble metal oxides in alkaline solutions [2].

Experimental/methodology. CFCO was synthesized by a sol-gel method containing a calcination procedure at 873 K [1]. Photoanodes were prepared by an electrophoretic deposition method (EPD). WO_3 was loaded on FTO substrates at 10 V and calcined at 723 K, then, CFCO was loaded on them at 2 - 5 V. Finally, the resultant CFCO/WO_3 were calcined at 873 K. The photoelectrochemical performances were investigated by using a normal three electrode system using the CFCO/WO_3, a Pt and a Ag/AgCl/KCl (satd.) electrode as the working, counter and reference electrodes, respectively. The solar simulated light was irradiated from the back side of the FTO glass. An aqueous solution was a neutral electrolyte containing phosphate.

Results and discussion. The amounts of CFCO gradually increased with increasing applied EPD voltage between 2 and 4 V, and drastically increased at 5 V. The photocurrent increased with increasing CFCO up to 3 V and decreased at more than 4 V. The saturated photocurrent density of CFCO/WO_3 loaded at 3 V came close to those of WO_3 with RuO_2. From cyclic voltammograms, saturated photocurrent of CFCO/WO_3 formed at 3 V was almost constant during cycling test for 10 cycles (Fig. 1a), whereas that of bare WO_3 rapidly decreased with increasing the cycles (Fig. 1b). From SEM images after the photoelectrochemical water splitting, the surfaces of WO_3 particles were maintained smooth by loading CFCO (Fig. 1c), whereas those of bare WO_3 particles became uneven and a lot of pits were formed (Fig. 1d). These results suggest that photocorrosion of WO_3 was suppressed by loading of CFCO, leading to improvement of stability.

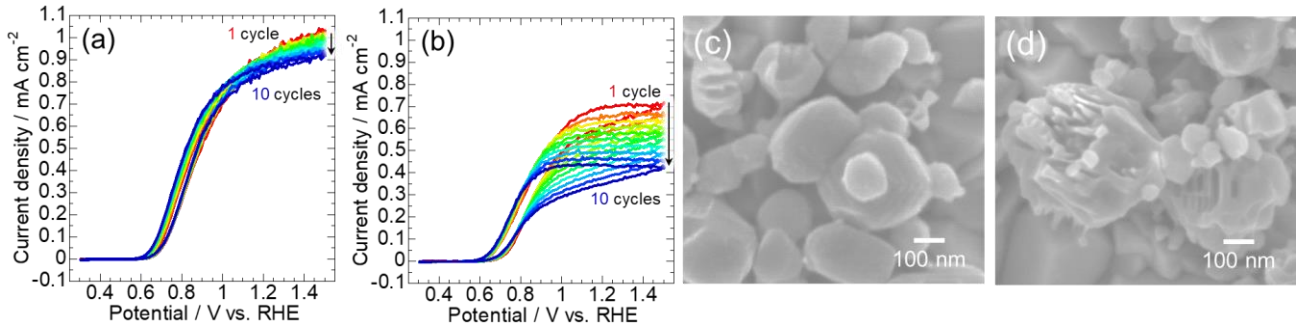

Fig. 1. Cyclic voltammograms of (a) CFCO/WO_3 prepared by the EPD method at 3 V and (b) bare WO_3. (c) and (d) shows SEM images of the CFCO/WO_3 and bare WO_3 after the stability tests.

Acknowledgments *A part of this study was supported by JSPS KAKENHI (22H02169), the Takahashi Industrial and Economic Research Foundation, Joint Usage/Research Center for Catalysis of Hokkaido University (22AY0147) and Advanced Research Infrastructure for Materials and Nanotechnology (ARIM, JPMXP1222HK0085) in Japan.*

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The role of water at the interface with TiO_2 for H_2 photoproduction

R. Verduci[1*], F. Creazzo[2], G. Cassone[3], F. Tavella[1], C. Ampelli[1], S. Luber[2], S. Perathoner[1], G. Centi[1], G. D'Angelo[1]

[1]*University of Messina, Messina, Italy*

[2]*University of Zürich, Zürich, Switzerland*

[3]*Institute for Chemical-Physical Processes, National Research Council of Italy (IPCF-CNR), Messina, Italy*

**rosaria.verduci@unime.it*

Introduction

Water molecules close to a charged solid surface play a crucial role in electrochemical processes. Indeed, the organization of interfacial water, which depends on the chemical composition and geometry of the catalyst surface, controls: i) the transport of ions and other molecular species and ii) the thermodynamics and kinetics of reactions (such as catalyst performances, activation energy and reaction rate) [1,2]. Thus, unravelling the structural and electrical organization of the electric double layer (EDL), *i.e.,* the region of water in the proximity of a solid surface, is fundamental for a deep knowledge of electrochemical processes and for the development of new and efficient catalysts [1,2]. Motivated by these reasons, in this work, by combining experimental and theoretical approaches, we provide new insights into the water network at solid interfaces and relate it to the electrochemical water splitting.

Experimental

Different TiO_2 (undoped and boron-doped) powders were synthesized. X ray diffraction (XRD), UV-vis, Raman and photoluminescence techniques were used to characterize the catalysts. The samples were tested for hydrogen production, and molecular dynamics simulations and highly accurate FTIR spectroscopic measurements were performed to obtain information about the arrangement of interfacial water.

Results and discussion

The rate of H_2 production over the B-doped TiO_2 is about 4.5 times higher than that of the other TiO_2 catalysts (Figure 1a). This result is related to the specific hydrogen-bond network of the water molecules which is strongly influenced by the morphology of the solid surface. Through the analysis of the FTIR spectra and, in particular, by probing the vibrational modes of water (OH stretching and HOH bending modes), we found five different water populations (an example is reported in Figure 1b) that change at varying the interface. The experimental results agree with the theoretical ones that suggest that the boron atoms never act as water-adsorption sites or as available surface sites for hydrogen-bonds formation. In addition, the boron atoms can tune the surface work function of TiO_2, enhancing interfacial reactions with the aqueous environment.

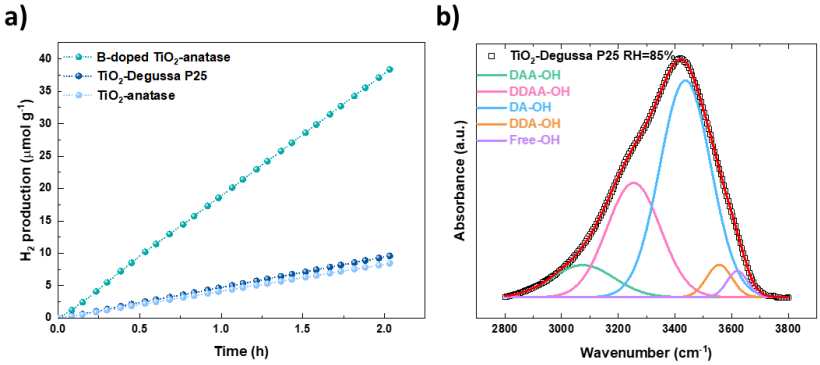

Figure 1: a) Hydrogen production (in µmol per gram of catalyst) versus time over the investigated TiO_2 catalysts, b) example of Gaussian deconvolution of the OH stretch band of TiO_2-Degussa P25/water system at RH=85%.

Acknowledgments

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Valorisation of glycerol wastewater for hydrogen production at pilot scale under natural radiation

J. G. Villachica Llamosas [1], A. Ruiz-Aguirre[1], S. Malato[1]
[1] *CIEMAT – Plataforma Solar de Almería, Ctra. De Senés s/n, 04200 Tabernas, Almería, Spain*
[*] *jgvillachica@psa.es.*

Hydrogen, as energy carrier, is gaining renewed and rapid attention in the world. However, hydrogen is still largely produced from fossil fuel. A renewable way for its production is photocatalytic water splitting, but the efficiency of this process is extremely low. An alternative is photoreforming of organic compounds, being glycerol, an abundant byproduct of biodiesel wastewater that allows wastewater revalorization[1]. To date, the maximum efficiency (Solar To Hydrogen efficiency (STH)) reached has been 5 % but with an unstable photocatalyst[2]. For that, great efforts in finding an efficient and stable photocatalyst is one of the major targets in this field. In this work, glycerol photoreforming was carried out in a pilot photoreactor (25 L) under natural solar radiation conditions. The photoreactor consisted of a stainless steel tank (10 L) coupled to a solar compound parabolic collector (CPC) (14.25 L of illuminated volume, 2.1 m^2 of illumined surface) in continuous recirculation (20 $L \cdot min^{-1}$). N_2 gas was bubbled in the system (max. flow rate of 500 $mL \cdot min^{-1}$) to keep anoxic conditions and also to entrain continuously the H_2 produced, from the head-space of the tank to the on-line gas chromatograph for quantification.

Different commercial and synthesis photocatalysts ($NiO:TiO_2$, $CuO:TiO_2$, gC_3N_4-urea, gC_3N_4-urea- CuO, gC_3N_4-melamine, gC_3N_4-Ru, C-Ru) were tested trying to reach the most efficient one varying the operating conditions (glycerol concentrations, catalyst concentrations, proportion of cocatalysts and soft calcination) in different water matrixes (demineralized water, natural water and artificial wastewater). Best results (1.44 % of STH) were achieved with TiO_2 mixed with metal oxides in a proportion of 10:1 respectively (Fig. 1). Tests performed under different irradiation conditions and different seasons of the year produced consistent results. Decontamination and disinfection in anoxic conditions, was achieved after 180 min and 10 min respectively. A soft calcination at different temperatures (200 ◦C and 400 ◦C) and times (1 h, 3 h and 6 h), was applied to the catalyst mixture ($CuO:TiO_2$) to increase its efficiency, achieving at 200°C temperature and 3 h calcination the best results (Fig.2). In natural water, the presence of salts reduced process efficiency requiring a higher concentration of photocatalyst .

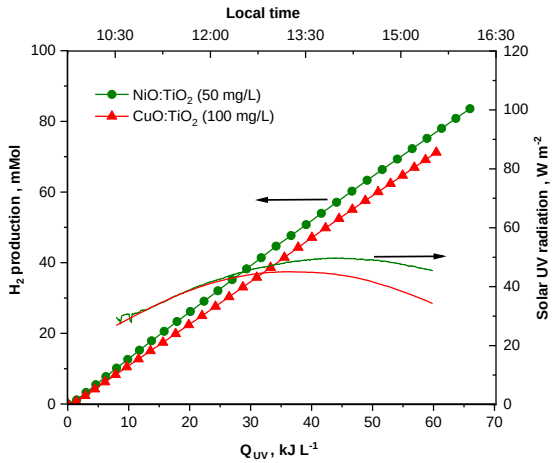

Fig.1. Hydrogen production with different commercial photocatalyst.

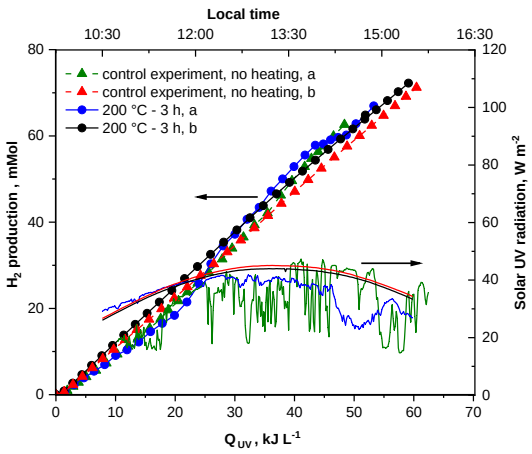

Fig.2. Evaluation of the application of soft calcination in the efficiency of $CuO:TiO_2$.

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Photocatalytic Water Splitting Using Strontium Titanate and Bismuth Vanadate in Twin Photoreactor to Simultaneous Separation of H_2 and O_2

Yu-Guan Lee[1], Jeffrey C. S Wu[1*], Marjeta Maček Kržmanc[2]

[1]*Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617*
[2]*Advanced Materials Department, Jožef Stefan Institute, Jamova 39, SI-1000, Ljubljana, Slovenia*
[*]*cswu@ntu.edu.tw*

Keywords: Photocatalytic water splitting, $SrTiO_3$, $BiVO_4$, Solar Hydrogen, Twin photoreactor

Introduction.
It is urgent to develop alternative energy sources to fossil fuels because of global warming and the energy shortage. Hydrogen has been widely studied as sustainable energy with broad application potential. Moreover, hydrogen production by photocatalytic water splitting is known as green hydrogen with zero-carbon emissions. However, the separation of H2 and O2 requires extra energy. This study provides an alternative to separate H2 during water splitting by a novel photo twin reactor [1].

Experimental/methodology.
$SrTiO_3$ was synthesized by the flux molten-salt method. $BiVO_4$ was prepared by the hydrothermal method [2]. In the twin photoreactor, $Rh_xCr_{2-x}O_3/SrTiO_3$ was used as the hydrogen-evolution photocatalyst, and $BiVO_4$ was used as the oxygen-evolution photocatalyst. Ferric/Ferrous ions served as electron media, and a cation-exchanged Nafion membrane divided the two photocatalysts in the twin photoreactor.

Results and discussion.
As shown in Figure, The rate of H_2 and O_2 were 204 and 110 μmol g^{-1} h^{-1}, respectively. The Z-system of the twin photoreactor can separate hydrogen and oxygen simultaneously during photocatalytic water splitting, thus not only avoiding the recombination of hydrogen and oxygen but also reducing additional separation costs and explosion risk. This research brings in the value of photocatalysts in practical applications.

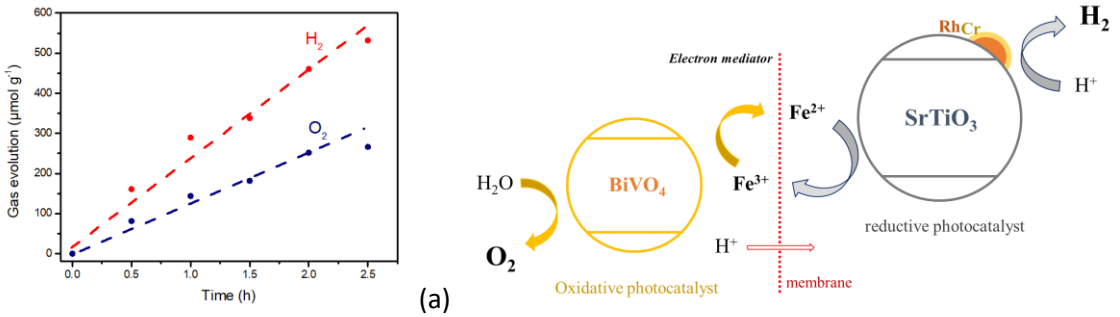

Figure: (a) H_2 and O_2 yields (b) Z-Scheme of photocatalytic water splitting

Acknowledgments
The authors gratefully acknowledge the Ministry of Science and Technology (MOST), Taiwan, for the financial support under grant number MOST 108-2923-E-002-006-MY3.M.M.K. acknowledges the Ministry for Education, Science, and Sport from Slovenia to provide support for M-era.Net project (SunToChem), under contract no. C3330-19-252011).

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Synthesis of $Co_2P/Cd_{0.9}Zn_{0.1}S$ by electrostatic attraction for enhancing H_2 Evolution

Yang Yang[1,2], Xiuzhen Zheng[2], Chun Cai[1*]

[1] Nanjing University of Science and Technology, Nanjing, P. R. China
[2] Huaibei Normal University, Huaibei, P. R. China
[*]*Corresponding Author's E-mail：c.cai@njust.edu.cn*

Keywords: photocatalytic H_2 evolution, electrostatic attraction, $Cd_{0.1}Zn_{0.9}S$ solid solution, energy barrier.

Introduction. Currently, the efficiency of solar energy conversion to H_2 is still far below the requirements of potential applications. To improve the photocatalytic activity of H_2 production, a novel Co_2P/ZCS shell-core photocatalyst were successfully synthesized by electrostatic attraction, with Co_2P layer covering on the surface of CZS sphere. This study focuses on the material design and strategies for improving the anti-photocorrosion of CdS-based photocatalysts, which provides an important reference basis for new catalyst design and wide prospects for further application in photocatalytic H_2 evolution.

Experimental/methodology. Co_2P decorated $Cd_{0.9}Zn_{0.1}S$ (CZS) nanocomposites was synthesized via a self-assembly method. A certain amount of Co_2P was added into absolute ethanol and ultrasonic treatment for 30 min. Subsequently, CZS was added into the above solution, and continuous ultrasonic treatment for another 30 min. To remove ethanol, the solution was directly dried at 60 ℃ for 12 h in a vacuum oven.

Results and discussion. A novel Co_2P/ZCS shell-core photocatalyst were successfully synthesized by self-assembly method, in which properly loading of Co_2P layer on CZS can improve the photocatalytic activity of H_2 production. Under visible light irradiation, CP-4/CZS achieves a H_2 yield of 16.5 mmol g^{-1} h^{-1} in $PhCH_2OH$ solution, much higher than CZS. The coating Co_2P layer can promote charge separation and transfer, and reduce the CZS oxidation caused by the aggregation of photogenerated h^+ on the CZS surface. Moreover, S-scheme heterojunction formed between Co_2P layer and CZS sphere effectively promotes the separation of photogenerated electrons and holes, improving the efficiency of photocatalytic hydrogen precipitation (**Figure 1**).

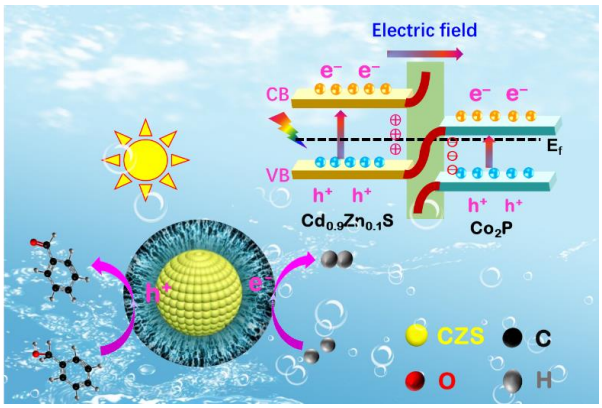

Figure 1. The S-scheme transfer mechanism of H_2 evolution on CP-4/CZS composite under the visible light.

Acknowledgments

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Catalytic technologies for liquid or solid waste reduction or purification

Mechanocatalytic Depolymerization of Plastics

Andrew W. Tricker,[1] Yuchen G. Chang,[1] Anuoluwatobi Osibo,[1] Karoline L. Hebisch,[1] Van Son Nguyen,[1] Carsten Sievers[1,*]

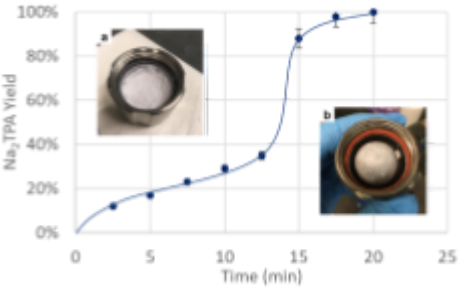
[1]*Georgia Institute of Technology, Atlanta, GA 30332, USA*
**carsten.sievers@chbe.gatech.edu*

Keywords: Ball mill, Plastics upcycling, Ammonia synthesis, Reactor design

Introduction. Mechanochemical processes use collisions in a ball mill or similar device to drive chemical reactions. The collisions can create transient surface sites with extraordinary catalytic activity and hot spots with rapid local temperature rises followed by dissipation of heat to the environment. Mechanically induced charge separation (i.e., triboelectric effect) and mechanoradicals formed by homolytic cleavage of polymers can also initiate reactions. In addition, mechanical forces can create intimate contact between two solids through shearing, so that the conversion of a solid reactant over a solid catalyst becomes viable.

Experimental/methodology. Milling experiments were performed in a Retsch MM400 vibratory ball mill with stainless steel vessels and balls. Milling vessels were modified to allow for continuous gas flow through the vessel. Gas flows were regulated with mass flow controllers. CO_2 formation was monitored by online MS analysis using a Hidden HPR-20. Monomers from plastics depolymerization reactions were analyzed by GC or HPLC, whereas GPC was used to measure the molecular mass distributions of the residual polymers.

Results and discussion. A fundamental study of hot spots on $CaCO_3$ showed that the impact of a 20 mm steel ball with a net velocity of 3 m/s results in a hot spot above 800 °C, which decays in 10s of ms. [1]. While the exact temperature profile depends on the impacted material, this illustrates reactive environments in mechanocatalytic processes.



The ability to shear different solids against each other opens new possibilities for converting solid feedstocks like waste plastics. The depolymerization of poly(ethylene terephthalate) (PET) occurred readily when the polymer was milled with NaOH [2]. After a short induction period in which particle size reduction dominated, monomers were produced at a constant rate up to a milling time of 12.5 min (Figure 1). At this point, the reaction mixture was converted from a powder into a wax that coated the milling balls or was pressed into the sites of the milling vessel (inserts in Figure 1). After wax formation, the remaining polymer was converted much faster. The molecular mass distribution of the residual polymer barely changed indicating that polymer domains are either entirely depolymerized or not affected at all. The reaction kinetics are consistent with a modified shrinking core model.

Mechanocatalytic depolymerization of poly(styrene) (PS) follows a radical mechanism. The presence of O_2 and certain metal catalysts increased the formation of active radical species. When the concentration of monomeric styrene in the milling vessel reached a threshold repolymerization to a more stable polymer occurred. However, when styrene was continuously purged from the reactor in an inert gas stream the rate of styrene production remained approximately constant with respect to milling time. The selection of suitable catalysts for this reaction will be discussed.

Poly(ethylene) is effectively depolymerized in a mechanocatytic process, in which some carbon atoms in the polymer chain are oxidized over an Fe_2O_3 catalyst to facilitate chain cleavage.

Acknowledgments
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Understanding of Fe reduction in the dechlorination of plastic waste derived pyrolysis oil using chlorobenzene as model compound

Ainara Moral[1*], Andrea Kjønli[1], Kumar Ranjan Rout[2], De Chen[1]

[1]*Norwegian University of Science and Technology (NTNU), Department of Chemical Engineering, Trondheim, Norway*

[2]*Quantafuel ASA, Oslo, Norway*

**ainara.moral.larrasoana@ntnu.no*

Keywords: Plastic waste, pyrolysis, dechlorination, iron

Introduction. The dechlorination of Cl containing hydrocarbons derived from the pyrolysis of plastic waste is a big challenge to overcome due to the strict requirement of Cl content permitted in the steam crackers (10 ppmw). Several strategies have been proposed to decrease the Cl content throughout the process. These include, stepwise pyrolysis, hydrodechlorination, "in-situ" dechlorination as well as the use of a subsequent gas cleaning step by different catalysts and/or sorbents. However, in most cases, a combination of different steps is required [1]. Among the studied materials for dechlorination step, Fe has been reported as very promising catalyst/sorbent to remove the Cl to the targeted values. Different Fe-based materials have been used including α-Fe_2O_3, γ-Fe_2O_3, Fe/C, α-FeOOH, Fe/SiO_2 or red mud [2]. It is known that the activity of the different phases and reduction state of Fe have a big influence in the dechlorination behavior. However, this has not been studied in depth in the literature. In addition, the dechlorination mechanism is still not clear. In this work, a synthetic Fe_2O_3/SiO_2 has been employed to investigate the effect of the reduction state, as well as try to clarify the reaction mechanism of Fe in the dechlorination using chlorobenzene (CB) as model compound.

Experimental/methodology. An Fe-based material supported on SiO_2 has been prepared by incipient wetness impregnation. To elucidate the reduction effect in the reaction, different reduction conditions, including different temperatures and reduction times have been studied. The reaction has been carried out in a quartz reactor using a 50 ppm CB/N_2 at 350 °C. Furthermore, to find the reduction state of iron in the different conditions, the materials have been characterized by TPR, "in-situ" UV-Vis spectroscopy and XRD before and after the reaction.

Results and discussion. The activity results showed a clear effect of the reduction temperature in the CB conversion (Fig 1 A), demonstrating that the most favorable reduction state appear with the reduction done at 350 °C for 2h. On the other hand, by XRD analysis of the fresh and spent samples (Fig 1 B), it was found different Fe crystal phases when different reduction treatment were employed. The fresh and unreduced spent samples contained Fe_2O_3. The spent sample reduced at 500 °C presented crystalline Fe^0 and the spent sample reduced at 350 °C appeared as an intermediate reduction mixture (Fe^0/Fe_3O_4) difficult to identify by XRD. These results suggest that the oxygen vacancies generated by the incomplete reduction may have an important effect in the dehlorination mechanism. Hence, "in-situ" characterization such as UV-Vis spectroscopy is clue to determine the Fe reduction degree in the reaction conditions.

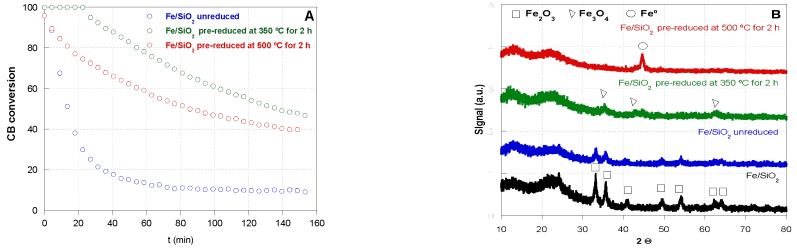

Fig 1. Chlorobenzene conversion during 150 min on stream with Fe/SiO_2 unreduced, reduced at 350 °C for 2 h and reduced at 500 °C for 2 hour (A), XRD diffractograms of fresh Fe/SiO_2 and after reaction (B)

Acknowledgments

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Succinic acid as central intermediate for the conversion of waste substrates to ethylene

Christian M. Pichler [1,2,3*], Subhajit Bhattacharjee[3] and Erwin Reisner[3]

[1]*Centre of Electrochemical and Surface Technology, Wiener Neustadt, Austria*
[2]*Institute of Applied Physics, Vienna University of Technology, Austria*
[3]*Yusuf Hamied Department of Chemistry, University of Cambridge, UK*
E-mail: christian.pichler@cest.at

Keywords: Electrocatalysis, Decarboxylation, Sustainable olefin production

Introduction. Ethylene is an important feedstock in the chemical industry that is currently produced from fossil resources. The electrochemical oxidative decarboxylation of carboxylic acids, such as succinic acid, can offer an environmentally friendly route to generate ethylene provided the electrolysis uses renewable electricity and the succinic acid is obtained from waste streams. We have developed two different approaches for this task. Firstly, a two-step process that can convert plastic waste into gaseous products, with ethylene as main product, that can be even used to resynthesize Polyethylene and offer a genuine chemical recycling route for plastics. Secondly, a bio-electrochemical approach allowing the conversion of food waste into ethylene. In both processes, succinic acid is a central intermediate that undergoes an electrochemical reaction to form the valuable ethylene product. With spectroscopical and electroanalytical approaches as well as quantum mechanical calculations, insights into the reaction mechanism could be gained as well. Furthermore, different electrocatalysts were tested and material characteristics, beneficial for the ethylene formation could be determined. The developed processes offer great potential for sustainable and the fossil resource free production of ethylene.[1]

Experimental/methodology. A range of electrochemical and spectroscopic approaches such as Koutecky–Levich analysis, rotating ring-disk electrode (RRDE) studies, and Tafel analysis as well as quantum chemical calculations, electron paramagnetic resonance (EPR), and in situ infrared (IR) spectroscopy generated further insights into the reaction mechansism. Different pre-treatment procedures (thermal and biocatalytic) were applied to make the heterogeneous substrates such as plastic waste or food waste accessible for electrochemistry. Finally, electrocatalytic tests in batch and flow cells were performed to convert the waste streams into alkenes.

Results and discussion. It was found that the nature of the carbon material significantly influences the reaction outcome and well-ordered, two-dimensional electrode materials are preferred, such as flat graphite. Electrochemical experiments and in situ IR spectroscopic measurements support the determination of the onset potential for the decarboxylation reaction ranging between 2.2 and 2.3 V vs. RHE. Insights into the reaction network were gained using quantum chemical calculations, and the presence of a monoalkyl radical as a reaction intermediate was confirmed by EPR spectroscopy. Finally, the utility of succinic acid to ethylene decarboxylation was exemplified by demonstrating a combined bio-electrocatalytic approach converting food waste into succinic acid and subsequently into ethylene (0.4 µmol ethylene cm^{-2} h^{-1}) and a thermal-electrocatalytic process converting plastic waste into ethylene.[2}

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Sustainable Olefin Metathesis: Catalytic Conversion of Persistent Plastics to Propylene

V. Farkas,[1] M. Nagyházi,[1] P. T. Anastas,[2] J. Klankermayer,[3] R. Tuba[1*]

[1]*Institute of Materials and Environmental Chemistry, Eötvös Loránd Research Network, Research Centre for Natural Sciences, P.O. Box 286. Budapest, Hungary*
[2]*Yale Center for Green Chemistry and Engineering, Yale University New Haven, Connecticut, 06511, USA*
[3]*Institut für Technische und Makromolekulare Chemie, RWTH Aachen University Worringerweg 252074 Aachen, Germany*
tuba.robert@ttk.hu

Keywords: Olefin metathesis, ISOMET, sustainable catalysis

Introduction. The rising concerns of plastic waste management require a variety of strategies and technologies to move towards sustainable and circular materials. One such strategy to address the challenge of persistent fossil-based plastics is new catalytic processes being developed to convert domestic plastic waste, such as polyethylene, to produce propylene. Morover, the propylene – the petrochemical produced in the second largest volume – can be an important precursor also to high-performance polymers that are biodegradable on-demand.

Results and discussion. Olefin metathesis is one of the most versatile methods in synthetic organic chemistry. Since the discovery of stable and functional group-tolerant catalyst systems, their industrial application has been steadily increasing. The isomerization metathesis (ISOMET) is a special case of olefin metathesis. [1] It is a one-pot, tandem reaction using a dual catalyst system. During ISOMET, the olefinic bonds migrate along the hydrocarbon chain (isomerization), which is followed by a metathesis reaction. Such simultaneous olefin isomerization and metathesis enables for example propylene synthesis from polyethylene waste or even from renewable feedstocks (vegetable oils, phospholipids). The presented method is based on the principles of sustainable development – in the same time, it lays the foundations for a unique, future-oriented research direction.[2]

Acknowledgments
R. Tuba is grateful for the Fulbright Scholarship (2022–2023) and for the Alexander von Humboldt Research Linkage Alumni program.

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Wet air oxidation of a refinery wastewater using catalytic materials synthesized from an oily sludge.

S. Jerez[1*], M. Ventura[1], M.I. Pariente[1], J.A. Melero[1]

[1]*Department of Chemical and Environmental Engineering, University Rey Juan Carlos, Madrid, 28933, Spain*
[*]*sara.jerez@urjc.es*

Introduction. A significant amount of residues are generated by the refinery industry that are highly toxic to human health. Refinery wastewater and oily sludge are considered environmentally hazardous and cost prohibitive in terms of management. Thus, valorising strategies should be developed to minimize their impact and enhance their reuse. The solid content in oily sludge is approximately 40 wt.%, with a high concentration of carbon material (45 wt.%). Several authors have reported promising results in the synthesis of porous materials using refinery residues, which can be used for several applications [1]. At the same time, some refinery wastewaters typically present a non-biodegradable and high organic content, and oxidative processes are commonly applied for pollutant removal. In the present work, the synthesis of a new class of materials using the solid particles of oily sludge, and its application in catalytic wet air oxidation (CWAO) reactions to treat a non-biodegradable refinery wastewater is proposed.

Experimental. The refinery wastewater and oily sludge come from the spent caustic effluent and API separator, respectively, of a refinery treatment plant in Spain. The solid fraction from oily sludge was mixed with KOH as an activating agent with 0:1 (ACT-0.1) and 1:1 (ACT-1.1) mass ratio and applied a carbonization (400 ^{0}C, 4 ^{0}C/min and 30 min) and activation (850 ^{0}C, 4 ^{0}C/min and 80 min) steps, both in N_2 atmosphere. CWAO reactions were carried out in an autoclave reactor, at 200 ^{0}C and 50 bar of air pressure for 4 hours, using 1 g/L of catalyst, and analysing the removal of chemical oxygen demand (COD) concentration of the refinery wastewater with the reaction time.

Results and discussion. The results obtained for the synthesis of these new materials have proved the feasibility of obtaining interesting materials with high carbon content (40 and 30 wt.%), metals (39 and 31 wt.%), and specific surface area (S_{BET}) ranging from 55 to 637 m^2/g for ACT-0.1 and 1.1 respectively. The use of KOH during the synthesis clearly increases the textural properties of the solids which implies an improvement of the catalytic activity up to 60 % of COD removal for the material ACT-1.1, compared with a 45% for the material ACT-0.1 (Figure 1). This catalytic performance was benchmarked with a commercial activated carbon (ACT-NORIT), with higher S_{BET} (1000 m^2/g). This material shows lower COD removal than ACT-1.1 despite its higher S_{BET} which is an indication of the significant contribution of metals in the catalytic abatement (mainly Fe with a 15 wt. %). Furthermore, a thermal WAO assay was carried out reaching less than 40 % of COD removal. This fact evidences the important role of synthesized materials in the COD removal. Moreover, the raw solid particles coming from the sludge were used as catalyst (ACT-Raw) showing a COD removal even lower than WAO reaction, probably due to the leaching of organic matter in the untreated solid. ACT-1.1. sample was reused in three catalytic cycles keeping the catalytic activity and without leaching of metallic species.

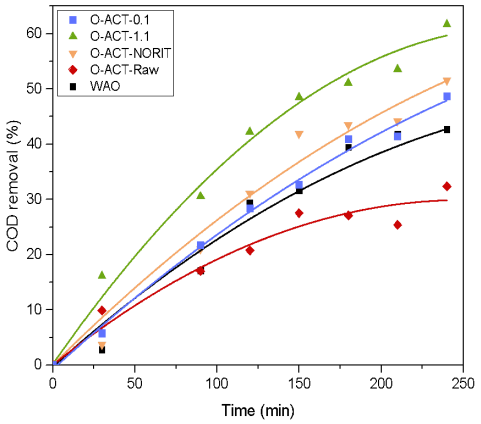

Figure 1: CWAO reactions using the synthetized catalysts (ACT-NP 0.1 and 1.1), a commercial activated carbon (ACT-NORIT), the raw solid particles (ACT-Raw) and a thermal wet air oxidation reaction without catalyst (WAO).

Acknowledgments

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Self-decontaminating protective clothes: Layer-by-Layer TiO_2 deposition for photocatalytic decontamination of Chemical Warfare Agents

Morguen Maël[1,2], Bacoup Stéphane[1], Vaure Louis[1], Keller Valérie[2*]

[1] *Paul Boyé Technologies, Labarthe-sur-Lèze, France*
[2] *ICPEES, Strasbourg, France*
[*] *vkeller@unistra.fr*

Keywords: Photocatalysis, Decontamination, TiO_2, Layer-by-layer, Textiles

The different challenges of the next decades may bring an increase in geopolitical tensions and thus a risk of conflicts accompanied by an eventual use of Chemical Warfare Agents (CWA). As a result, protections against CWA need to be improved and the addition of self-decontaminating properties to military clothes is a promising tool to avoid (cross-)contamination issues. The purpose of this work is to develop photocatalytic textiles capable of degrading CWA and more specifically organophosphorus compounds under light activation. For this purpose, TiO_2 has proved to be an efficient photocatalyst for CWAs degradation under UV-A irradiation [1]. However, its immobilization on textiles remains a challenge due to its poor adhesion on fibers for more convenient post-synthesis functionalization. For this reason, we decided to use a layer-by-layer deposition method consisting in an alternative deposition of positively charged particles (pH below isoelectric point) and negatively charged polymers (intrinsic properties) [2]. This method enables both a control of the thickness of the photocatalytic layer, as well as a strong adhesion on fibers.

Many parameters of this deposition method can influence the overall activity through the amount of deposited TiO_2, such as the number of layers, and the concentration and pH of the TiO_2-based precursor suspension. A parametric study was performed to find the optimal conditions for a compromise between a good adhesion and a high photocatalytic activity. The nature of TiO_2 can also largely influence the activity with differences in some key properties such as specific surface area, surface properties, structure, band-gap, and efficiency of charge carriers generation [3]. For this reason, different commercially available TiO_2 were used for textiles functionalization and assessed towards DMMP (analog of organophosphorus agent) elimination for similar deposition conditions.

As expected, the quantity of TiO_2 deposited onto the micrometric fibers has a clear influence on the photocatalytic activity **(Fig. 1)**. Another impacting parameter lies also in homogeneity of TiO_2 deposition and adhesion onto the fibers **(Fig. 2)**. Differences in terms of resulting photocatalytic activities were also observed between the different commercial TiO_2 studies and will be explained and discussed. As new perspectives for the elaboration of self-decontaminating textiles, some examples relating the combination of TiO_2 with adsorbent materials, enhancing overall decontamination properties will also be shown.

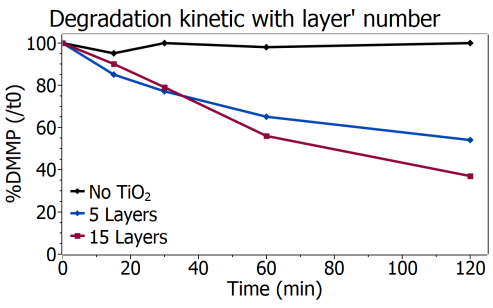

Fig. 1: Kinetics of DMMP elimination as a function of the number of deposited TiO_2 layers

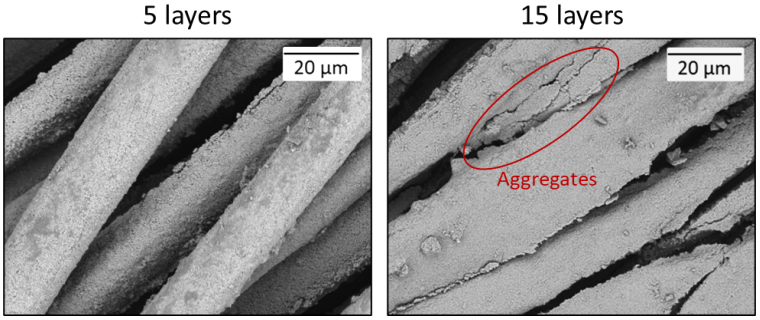

Fig. 2: SEM images of functionalized textiles with 5 and 15 TiO_2 layers.

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Catalyst and reactor design for high-throughput photocatalyst screening for degradation of female hormones in water

Sabine Schmitz-Stöwe[1*], Tony Benjamin Engelhardt[1], Minrui Zhu[1], Thomas Schwarz[1], Klaus Stöwe[1]

[1]*Chemnitz University of Technology, Chemical Technology, Chemnitz, Germany*
[*] *sabine.schmitz-stoewe@chemie.tu-chemnitz.de*

Keywords: photocatalysis, microslit reactor, parallel reactor, TiO_2, hormone, degradation

Introduction. In modern water management endocrine disrupting chemicals (EDCs) like pharmaceutical products or biocides are more and more in the focus of interest. This is, because in common three-stage sewage treatment plants these chemicals are not degraded in a sufficient degree or manner. Therefore, the German Federal Environmental Agency demands of a fourth cleaning stage to eliminate these substances. Existing solutions for the problem are taint with diverse disadvantages, e.g. that resulting decomposition products are sometimes more toxic than the pollution educts [1]. An alternative concept will be the catalytically supported degradation of these substances by UVA light. Here we present the photocatalytic degradation of artificial female hormones (EE2 = 17α-ethinyl estradiol) in aqueous model solution using two different reactor concepts. The objective is to invent a modular UVA-LED photoreactor system in combination with a special catalyst material having a tailored band gap according to the used UV wavelength of 365 nm [2,3,4]. The modularity of the concept allows adaptation to local wastewater qualities and quantities of small polluters and is not intended for application in municipal wastewater treatment plants.

Experimental/methodology. For high-throughput catalyst screening a 60-fold parallel UVA-LED reactor device was build up to simultaneously investigate the performance of different catalyst materials according to EE2 degradation. The syntheses of catalysts were performed either by sol-gel route or by wet-impregnation. All investigated ternary catalyst compositions are oxides with main component Ti and different amounts of doping elements. The catalysts were characterized by BET, IR and XRD-measurements. After catalyst screening the most promising catalyst candidates were processed as wall-catalyst for the useage in a modular designed microslit photoreactor with exchangable catalyst substrates. Degradation processes were tracked by SPE-GC-MS or UHPLC-TQ-MS.

Results and discussion. The selection of metal ions for the TiO_2 doping was made by looking at the band-gaps of the metal oxides. According to this Zn, Sn, Zr, Nb, Ce, W, Bi and Fe were chosen as doping metal candidates. Additionally g-C_3N_4 has been prepared and used as dopant. Compared to the benchmark of TiO_2 (P25) only Zn- or g-C_3N_4-doped TiO_2 lead to a higher degradation conversion. The performance was strongly depending on the preparation of catalyst material as particles for the parallel reactor or as coating in the microslit reactor, where the modified residence time plays an important role. The extensive testing of catalysts led to the conclusion that the photocatalytic conversion in the microslit reactor is limited by mass transport and thus rather a function of residence time than a function of the materials utilized. This makes adequate process development seem more important than material development. The novelty of this contribution lies in the unique combination of testing a wide range of composite catalysts in a unique microreactor geometry.

Acknowledgments
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Insight into reactivity of niobia-based catalysts in activation of hydrogen peroxide and degradation of organic pollutants

L. Wolski[1*], K. Sobańska[2], A. Walkowiak[1], J. Gryboś[2], M. Frankowski[1], M. Muńko[3], A. Czerniak[3], M. Ziolek[1], P. Pietrzyk[2**]

[1]*Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland*
[2] *Faculty of Chemistry, Jagiellonian University, Poland*
[3] *Center for Advanced Technology, Adam Mickiewicz University, Poznań, Poland*
[*]*wolski.lukasz@amu.edu.pl, **piotr.pietrzyk@uj.edu.pl*

Keywords: Advanced oxidation processes, reactive oxygen species, organic dyes, antibiotics

Introduction. For the last decades, Nb_2O_5 has been attracting attention as a promising heterogeneous catalyst dedicated to the elimination of organic pollutants through advanced oxidation processes (AOPs) [1]. Nowadays, the interest in the application of this metal oxide for wastewater remediation is still increasing and focuses on improving niobia reactivity by designing novel heterostructure catalysts and/or modifying its surface properties by post-synthetic modification or metal doping [1]. This work will summarize our recent studies aiming at understanding and improving reactivity of niobia-based catalysts in the catalytic activation of hydrogen peroxide and degradation of selected organic compounds. Particular attention will be paid to unraveling the role of niobia crystallinity [2] and the presence of metal [3,4] or nonmetal [5] dopants in controlling the efficiency of Nb_2O_5 in activating of H_2O_2 toward the formation of various reactive oxygen species (ROS). The reactivity of these strongly oxidizing species in the degradation of model organic pollutants (organic dyes and antibiotics) will be discussed.

Experimental/methodology. The studied oxidation catalysts were synthesized using co-precipitation or hydrothermal methods. The catalysts were fully characterized using XRD, FT-IR, UV-vis, XPS, TEM/EDS, N_2 physisorption, elemental analysis, and Zeta potential measurements. ROS formed *in situ* in the presence of hydrogen peroxide were identified with Raman and EPR techniques. The contribution of selected ROS to the degradation of organic compounds was estimated with the use of ROS scavengers. The degradation pathways and products were identified using ESI-MS and LC-MS analyses, while the mineralization efficiency was estimated based on Total Organic Carbon analyses.

Results and discussion. Our study revealed that the reactivity of Nb_2O_5 in H_2O_2 activation is strongly affected by the phase composition of the metal oxide. The highest efficiency in ROS formation is observed for amorphous niobia under acidic conditions [2]. We have also revealed that the catalytic decomposition of H_2O_2 proceeds via an electroprotic mechanism, resulting in the formation of $HO^{\bullet}$ radicals and $O_2^{\bullet-}$ radical anions. The latter can be adsorbed and stabilized on the niobia surface improving the efficiency of $HO^{\bullet}$ formation. We have also shown that ROS formed and adsorbed on the surface of niobia are responsible not only for the efficient degradation of pollutants but also for significant improvement of the adsorption properties, which has been overlooked so far. In a short reaction time, the contribution of surface ROS to the adsorption was found to be much higher than that to degradation [6]. We have also revealed that the reactivity of Nb_2O_5 in the degradation of organic pollutants (model dyes and antibiotics) via AOPs may be significantly enhanced by doping with Ce [3], Co [4], and P [5]. Electronic and structural factors resulting in the enhanced reactivity of these mixed systems have been discussed in detail.

Acknowledgments
This research was financially supported by the National Science Center, Poland (NCN), grants Sonatina2 (no. 2018/28/C/ST5/00255) and Sonata Bis7 (no. 2017/26/E/ST4/00794).

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Lignin Oxidation towards High-Added-Value carboxylic acids under mild hydrothermal conditions using MgO-based catalysts

N. Vidal*, M. Ventura, F. Martínez, J.A. Melero

Chemical & Environmental Engineering Group, Universidad Rey Juan Carlos, Mostoles (Spain)
**nora.vidal@urjc.es*

Introduction. Lignocellulosic biomass mainly consists of cellulose, lignin, and hemicellulose but lignin is the only sustainable aromatic resource in nature. Oxidation is one of the promising strategies that can convert lignin into a range of high-added-value platform chemicals. Because of the intrinsic complexity of the lignin polymer its oxidation is largely influenced by operation conditions, catalyst types, presence of oxidants, and solvent species.[1] One of the high-value-added products potentially obtained from this oxidation are the dicarboxylic acids (e.g., fumaric and succinic acids), which can be used as polymer building blocks [2]. Recently, in our research group, we have explored the catalytic oxidative-depolymerization of lignocellulosic wastes by using cheap and earth-abundant metals based on Ca-Mg [3] being not selective in the oxidation of the polymers. This work, explore the selective depolymerization of lignocellulosic wastes by using mixed oxides based only on Mg with improved properties that gives to a selective depolymerization of lignin to carboxylic acids.

Experimental/methodology. Different MgO catalysts were synthesized from different techniques and precursors: by co-precipitation method with $Mg(NO_3)_2$, by rehydrated $Mg(OH)_2$ and by xerogel and aerogel method using $Mg(C_2H_5O)_2$ as precursor To modulate the behavior of MgO the incorporation of MgO to SBA-15 was studied by two methods: adding Mg precursor during the SBA-15 synthesis (MgO-SBA-15) and by wet-impregnation of MgO over SBA-15 (MgO/SBA-15). The reactions were performed in a 15 mL ace pressure glass tube stirred with a magnetic bar; 0.1 g of the lignocellulose material, 20% wt. /wt. of catalyst and 5 mL of H_2O at 120 ^{0}C. The liquid phase was analyzed by HPLC to determine the catalytic performance and reaction products, whereas the remaining solid phase was characterized by elemental analysis and TGA to assess the conversion of the three polymers.

Results and discussion. All of the MgO catalysts are obtained with a crystalline structure (100), while for aerogel production from $Mg(C_2H_5O)_2$, the structure is (111). The total solid conversion results do not differ much between different catalysts being between 23 % and 38 %. However there are significant differences on the individual conversion of the three polymers, (Fig.1). The highest and most selective conversion of lignin was obtained with the catalysts synthesized from $Mg(NO_3)_2$, achieving over 1 g/L of dicarboxylic acids. MgO/SBA-15, was also very selective to convert lignin but not in a selective manner. Therefore, the catalyst that provides better results would be the MgO obtained by co-precipitation method from $Mg(NO_3)_2$, giving a residual solid mostly composed of cellulose and hemicellulose. The catalyst leaching was also analyzed during the reaction by ICP-AES and no loss of magnesium was observed. Catalyst showed a good catalytic performance after several catalytic cycles. Catalysts were fully characterized by XRD, SEM, ICP-AES and CO_2/NH_3-TPD.

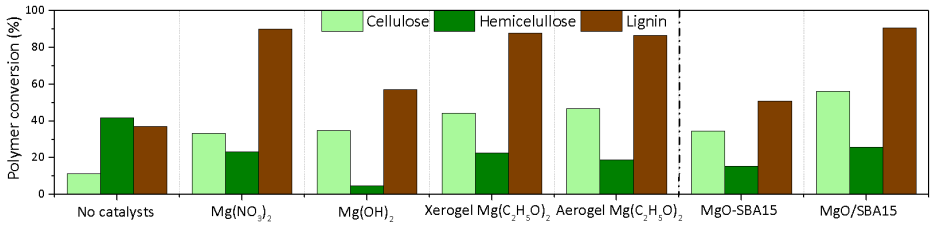

Fig. 1. Catalysts screening: polymers conversion

Acknowledgments

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Dechlorination of PVC to HDPE: Effects of Catalysts and Bases

S. Svadlenak[1], Dorthe Wildenschild[1], K. Goulas[1*]

[1]*Oregon State University, Corvallis, OR, United States of America*

Keywords: upcycling, polymers

Introduction. Polymer upcycling to value-added products is a necessary step for the reduction of pollution from waste polymers. While significant advances have been made towards successful upcycling of polyolefins to monomers and to liquid fuels and chemicals, processes to upcycle polyvinyl chloride (PVC) to useful chemicals are still largely elusive. The need for such a process is particularly important, as PVC represents a significant portion of the total mass of polymer that is landfilled around the world. Moreover, the presence of PVC in polyolefin waste streams complicates the upcycling of these waste streams, as residual chloride poisons catalysts and generates HCl and toxic chlorinated hydrocarbons. We propose to upcycle PVC to HDPE (high-density polyethylene), appropriate for use in hot melt adhesives, via a hydrothermal tandem dechlorination and hydrogenation process.[1]

Experimental/methodology. PVC resins and PVC-containing wastes are mixed with aqueous solutions of organic bases and a heterogeneous catalyst. The system is pressurized with hydrogen gas and heated to the reaction temperature. The product is analyzed by differential scanning calorimetry (DSC), FT-IR spectroscopy and NMR to obtain its yield and melting point. The reacted system is also analyzed by X-ray tomography, to understand how the gaseous, liquid and solid phases interact.

Results and discussion. We show that the yield of polyethylene increases with the Kow of the amine base used in the reaction. We attribute this increase to the increased partition of amine into the PVC phase, enabling homogeneous dechlorination. The resulting poly-ene molecule then undergoes hydrogenation over the Pt-based catalyst. This hydrogenation reaction competes with the hydrogenolysis of the product to short-chain hydrocarbons. Screening of multiple heterogeneous catalysts shows that Pt is the optimal catalyst, showing the highest yield and a satisfactory melting point. Hot melt adhesives require waxes with melting points between 80 and 130 °C. Further improvements in yield and melting point can be achieved by using alloy catalysts.

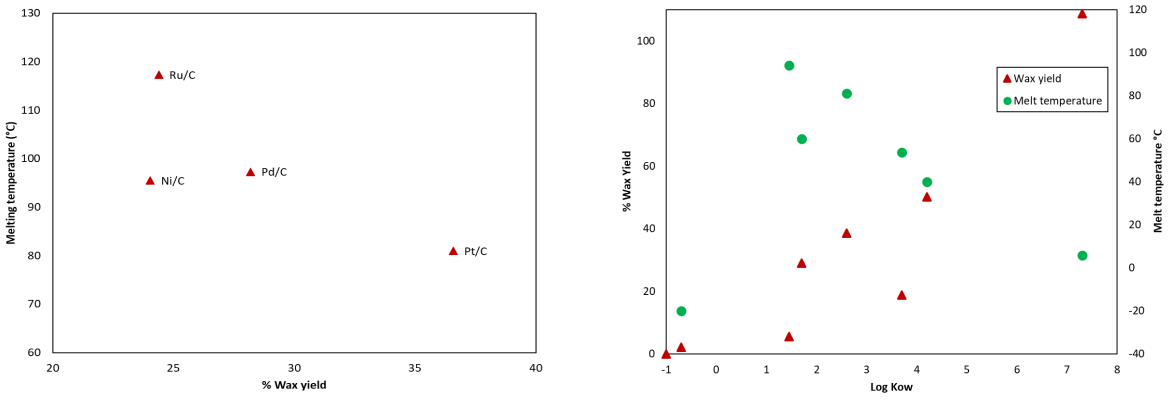

Figure 1: Effects of the amine base (left – Pt/C catalyst) and of the metal catalyst (right – N,N-dimethylhexylamine base) on the yield and wax melt temperature. 200 °C, 33:1 PVC:metal (by mass). 24 hr, 5.5 bar H_2, 200 °C 3:1 N:Cl ratio

Acknowledgments

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Acidic carbocatalyst for the conversion of polyethylene waste to hydrocarbons

M. Al-Naji[1*], M. Antonietti[1]

[1]*Max Plank Institute of Colloids and Interfaces, Colloid Chemistry, Am Mühlenberg 1, 14476 Potsdam, Germany,*
**majd.al-naji@mpikg.mpg.de*

Introduction. In 2021 it was estimated the European Union's production and consumption of plastics (fossil-based plastic, post-consumer recycled plastics, and bio-based plastics) to be 57.2 Mtons.[1] Of these large amounts of plastics, only ~12% are recycled, mainly mechanically.[1] Thus, there is a great demand in implementing new chemiocatalytic technologies to increase the number of recycled plastics. Recently, several chemical recycling techniques have been reported, *i.e.*, pyrolysis, hydrocracking, dissolution (mainly with sorted polymers), and gasification (energy intensive with low atom efficiency).[1] Of these, pyrolysis and hydrocracking are largely studied as they are promising approaches for non-sorted plastic waste composed of different polymer types and impurities.[1,2] Usually these methods describe the use of expensive bifunctional catalysts based on noble metal catalysts and acidic support materials, e.g., zeolites. Additionally, most of the recent publications use clean polymers, with a high catalyst/feed ratio.[1,2] All ordinary catalysts used in plastic waste recycling are suffering from rapid deactivation under these harsh conditions.[2] Therefore, we present a highly acidic carbocatalyst (AC) for polyethylene fragmentation to liquid hydrocarbons (C7-C20) that can be converted to olefins in a steam cracker for further processing.[2]

Experimental/methodology. This AC is synthesized by condensing a mixture of Na-lignosulfonate (sulfur-rich carbon source) and a hard template (ZnO) to generate porosity. All catalytic experiments in an inert atmosphere were performed in a 250 cm^3 round bottom flask connected to a condenser. The fragmentation of HDPE in the presence of 20 bar (H_2) was conducted in a 300 cm^3 stainless-steel batch reactor.

Results and discussion. The synthesized AC exhibits a high specific surface area (A_{BET} = 664 m^2 g^{-1}), as well as a high density of acid sites (1.6 µmol g^{-1}) that is attributed to the presence of an oxidized sulfur species, similar to electron-poor sulfones. Furthermore, this AC possesses high thermal stability due to the high content of (oxidized) sulfur (7.9 wt.-%) with oxygen edge terminations, which changes the electron density of the carbonized material and creates a “nobility”. For polymer fragmentation, the AC was then contacted with commercially available high-density polyethylenes (HDPE), as well as with a real waste plastic consisting of (LDPE and HDPE) from a sorting plant. In this context, the AC showed a high activity in HDPE fragmentation to (C7-C20) of n-alkane (348 mg g^{-1}_{HDPE}) and n-alkene (110 mg g^{-1}_{HDPE}) at 653 K and after 24 h of reaction time under N_2 atmosphere (Fig. 1). This indicates that the AC possesses dual functionalities namely acid sites for cracking C-C bonds and hydrogenation function. For stronger evidence of the superior activity of the AC and the existence of the dual functionalities, an experiment with externally supplied 20 bar of H_2 for 24 h was performed. The n-alkane yield was found to be 1302 mg g^{-1}_{HDPE}, while the n-alkene yield was suppressed and corresponded to 188 mg g^{-1}_{HDPE}. Additionally, the presence of external H_2 resulted in gas and oil fractions with product distribution rich in shorter n-alkanes in the range of C7-C14, with respect to H_2-free experiments (C11-C17), *viz.* Fig.1.

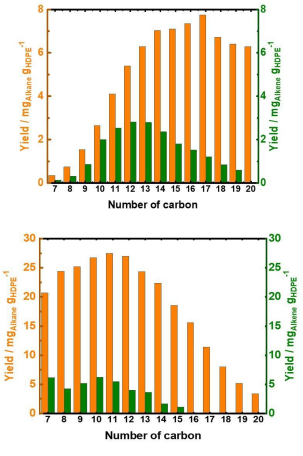

Fig. 1. Product distribution in the oil phase at from HDPE fragmentation for 24 h; Reaction conditions: m_{HDPE} = 5 g, $m_{catalyst}$ = 0.5 g, T = 653 K, n = 600 rpm, under N_2 (top) and 20 bar H_2 (bottom).

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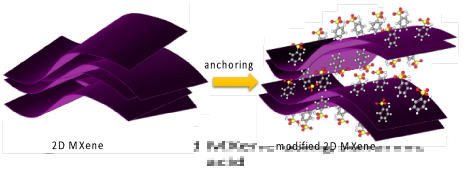
Catalytic PET depolymerization by hydrolysis using sulfonated 2D MXenes

Iuliana M. Chirica[a,b], Ștefan Neațu[a], Anca Mirea[a], Michel W. Barsoum[c], Mihaela Florea[a], Florentina Neațu[a,*]

[1]*National Institute of Materials Physics, 405A Atomistilor Street, 077125 Magurele, Romania*
[2]*University of Bucharest, Faculty of Physics, 405 Atomistilor Street, 077125 Magurele, Romania*
[3]*Department of Materials Science and Engineering, Drexel University, Philadelphia, USA*
*florentina.neatu@infim.ro

Introduction. One of the urgent currently ecological issues are related to the environmental concerns arise from polymer recycling that thrown a shadow over the importance of these materials that have an important role in our economy and daily lives. Heterogeneous catalysis plays a critical role recycling of waste plastics, but to date, none of these have demonstrated outstanding performance and this is why for this process, a viable industrial approach has not yet been developed [1,2]. Consequently, the ultimate goal of this study is to find new solid acids able to depolymerize PET to the raw materials. A potentially useful approach to control MXenes' catalytic activity [2,3] is to handle their surface chemistry. Therefore, during this study we intend to increase the MXenes acidity by modifying the surface with acidic moiety to have –SO_3H–MXene capable to depolymerize the polyethylene terephthalate (PET) by hydrolysis route.

Experimental/methodology. The goal of this study is to find new solid acids able to depolymerize PET to the raw materials. Among newly discovered materials, MXenes, a novel family of two-dimensional (2D) metal carbides-nitrides, with graphene-like structures, produced by etching of A element from MAX phase [2,3] has drawn our attention. A potentially useful approach to control MXenes' catalytic activity is to manipulate their surface chemistry. Therefore, during this study we extended the material acidity by modifying the surface with acidic moiety to have –SO_3H modified MXene (Figure 1) capable to depolymerize PET by hydrolysis.



Results and discussion. Modified MXene with sulfonated groups was realized by grafting –SO_3H groups using sulfonated aryl diazonium salt of sulfanilic acid. Different amounts of sulfanilic acid salt were used, in order to establish the influence of the sulfonic group concentration on the surface, denominated as $Ti_3C_2T_x$–SO_3H–y, where y=(1, 3, 5, 7). The as-modified MXenes were investigated by different techniques (XRD, DRIFT, RAMAN, SEM, TEM) and demonstrate that the MXene structure remains lamellar and did not collapse during sulfonation reaction. The distance between sheets increases after modification (see Figure 2) due to the aryl sulfonate groups anchored between the MXene layers. EDX (SEM) and XPS result have confirmed the presence of –SO_3H groups on the MXene surface. The use of these materials in PET hydrolysis depolymerization showed complete conversion and a yield of 75% terephthalic acid, with terephthalic acid as only reaction product. The influence of the reaction parameters (*i.e.,* temperature, pressure and amount of catalyst) was also studied and indicated that Ti_3C_2Tx–SO_3H-y are promising candidates for processing efficiently PET in environmentally friendly conditions.

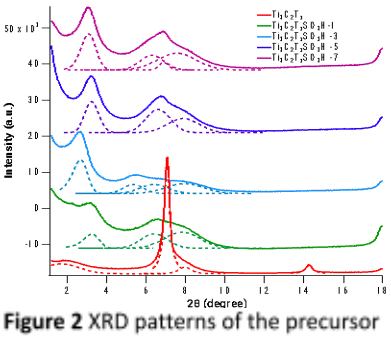


Figure 2 XRD patterns of the precursor MXene and sulfonated MXene

Acknowledgments

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Degradation of pharmaceuticals in water by combined ozonation and catalytic technologies: Metoprolol

S. Saeid[1, 2], P. Tolvanen[1*], A. Lahaye[1,3], P. Eklund[1], M. Kråkström[1], N. Kumar[1], T. Salmi[1]

[1]*Åbo Akademi University, Turku, Finland* , [2]*California Institue of Technology, Pasadena, United States*
[3]*École nationale supérieure de chimie de Rennes (ENSCR), France*
[*]*pasi.tolvanen@abo.fi*

Keywords: wastewater treatment, metoprolol, ozonation, heterogeneous catalyst

Introduction. Among emerging contaminants, pharmaceuticals represent a significant concern due to their toxicity and potential to harm aquatic species and humans. Biomagnification, bioaccumulation, and antibiotic resistance are the major negative effects of these contaminants [1]. As the water contamination steadily increases, scientists are searching for methods to improve wastewater treatment. A variety of chemical, physical, and biological wastewater treatment methods are used to remove pharmaceutical pollutants. However, the majority of these methods are expensive, have low effciency, and can even produce toxic waste products [2]. Using solid catalysts in advanced catalytic ozonation enhances the breakdown of ozone molecules, producing highly reactive free radicals. As a result, various organic compounds are degraded and mineralized quickly and efficiently [3]. Metoprolol is a beta blocker which is used in large amounts for heart and blood circulation diseases. Recent research has revealed that metoprolol medication can reach up to µg/L levels in surface waters, since conventional water and wastewater treatment processes have a very limited removal efficiency of less than 10%, posing a risk to human health and the aquatic environment [4]. We have developed a combined ozonation and catalytic method to effectively and completely eliminate this pollutant and several other pharmaceutical pollutants.

Experimental/methodology. We investigated the effects of some of our in-house, fully characterized Iron modified catalyts (Fe-H-Beta-25-EIM, Fe-H-Beta-75-SSIE, Fe-SiO_2-EIM and Fe-Al_2O_3-EIM) on the ozonation of metoprolol (MET). In order to perform the experiments, a new type of a gas-liquid reactor system was designed and constructed. By applying an ozone generator, ozone is created and fed into the liquid phase at the bottom of the reactor. The pharmaceutical solution is stirred vigorously while ozone-rich gas continuously bubbles through it. A special rotating bed device was used for the catalyst. The method allows for a very precise measurement of the decomposition kinetics of MET and its by-products.

Results and discussion. Ion trap mass spectrometry can identify MET by-products formed during ozonation. Seven different by-products are produced as a result of the ozonation of MET (Figure 1). In most cases, the catalysts enhanced the complete degradation of MET as well as its harmful by-products. For instance, Figure 2 demonstrates the degradation of the by-product 208 through catalytic vs. non-catalytic ozonation.

Figure 1: Noncatalytic Decomposition of metoprolol

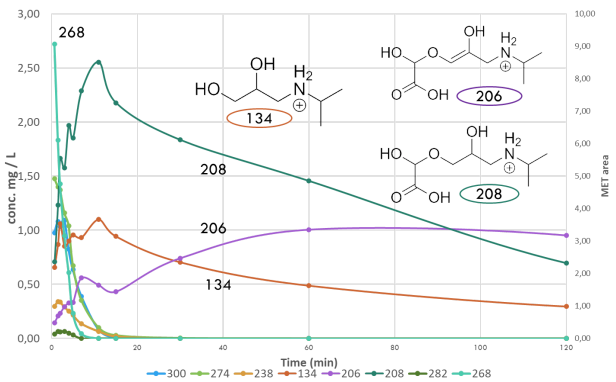
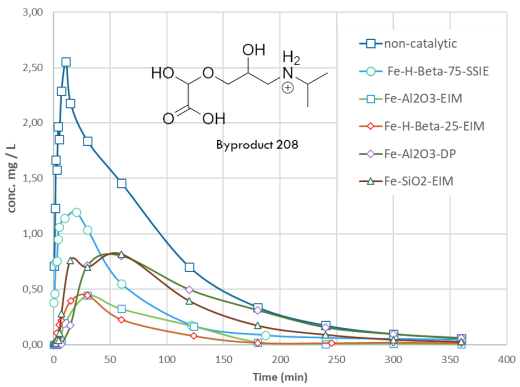


Figure 2: Decomposition of by-product m/z 208



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Composite and mixed oxides for degradation of water pollutants with H_2O_2 or peroxosulfates – generation of reactive species and catalytic activity

K. Sobańska[1], L. Wolski[2], J. Gryboś[1], D. Mucha[1], P. Leśniewska[1], M. Frankowski[2], P. Pietrzyk[1]*

[1] *Faculty of Chemistry, Jagiellonian University, Poland*
[2]*Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland*
[*]*piotr.pietrzyk@uj.edu.pl*

Keywords: Advanced oxidation processes, reactive oxygen species, oxides,

Introduction. Advanced oxidation processes (AOP) are a group of wastewater treatment techniques based on the generation of reactive oxygen species (ROS). ROS are highly active oxidizing agents that can be used for the degradation and mineralization of emerging organic pollutants. The most efficient ways to produce ROS are the decomposition of H_2O_2 or peroxosulphate anion in the presence of redox-active transition-metal oxides (through the Fenton-like mechanism) or the d^0 group of transition-metal oxides, which are redox-inactive under ambient conditions, yet are capable of activation of the peroxo bond via the electroprotic mechanism [1]. In this work, the reactivity of selected one-phase crystalline and amorphous oxides, binary crystalline-amorphous composites of these oxides, and resulting mixed oxides have been studied in the generation of ROS and sulphate radicals. Particular attention has been paid to the elucidation of the reaction mechanisms of the formation of reactive species and its role in the degradation of model organic pollutants (organic dyes and antibiotics).

Experimental/methodology. The materials obtained were synthesized using co-precipitation or hydrothermal methods and thoroughly characterized using XRD, FT-IR, UV-vis, XPS, TEM/EDS, N_2 physisorption, elemental analysis, and Zeta potential measurements. Various active species such as hydroxyl radicals ($^{\bullet}OH$), superoxide radicals ($O_2^{-\bullet}$), peroxide anions (O_2^{2-}), and singlet oxygen ($^1O_2$) were detected by EPR, Raman, and UV-vis spectroscopic techniques. In the case of EPR measurements, radicals were detected directly or indirectly using DMPO as a spin trap.

Results and discussion. The applied characterization techniques revealed that the obtained materials can be categorized into three generic groups: (1) amorphous-crystalline composites (e.g. $CuO@Nb_2O_5$, $Co_3O_4@ZrO_2$), for which the component phases preserve their initial nature (amorphous ZrO_2 and Nb_2O_5 supports and crystalline nanosized oxides of redox activity CuO, Co_3O_4, Fe_2O_3), (2) binary mixed oxides forming new crystalline phases ($CeO_x@Nb_2O_5$ forming the $NbCeO_4$ crystal phase), (3) dopped binary oxides ($NbCeO_x$-CuO_x, $NbVO_x$-PO_x). Spin-trapping studies proved that all investigated systems are active in the generation of hydroxy radicals and superoxide anion radicals (including pristine amorphous phases), while groups (2) and (3) participate in the generation of the hydroxyl and $SO_4^{-\bullet}$ radicals. This observation was confirmed by UV-vis studies of OPD oxidation. The presence of singlet oxygen was detected particularly in the case of phosphate-dopped systems [2]. Finally, the catalytic activity of the investigated oxides in methylene blue (MB) discolorations and ciprofloxacin (CIP) degradation was tested. The observed activity was accounted for by the concerted action of adsorption and oxidative degradation by reactive species (the competing impact of radicals and $^1O_2$ was unraveled in this case). In most cases, the catalysts make use of both electroprotic and Fenton-like mechanisms for the generation of reactive species. It is noteworthy that the $NbCeO_x$ mixed oxide is also active in the generation of $SO_4^{-\bullet}$ species with activity smaller than in the case of the amorphous Nb_2O_5, suggesting that the electroprotic mechanism of peroxo bond rupture is possible not only for H_2O_2 [1] but also for peroxosulphate substrate.

Acknowledgments
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Performance of Al/Ga-MFI Nanosponges and Nanosheets in the catalytic pyrolysis of biomass and plastics

F. Artillo[1], Y. Zhang[2], M. Alonso-Doncel[1], M. Mazur[2], P. Pizarro[1,3*], K. Kalíková[2], J. Čejka[2], D.P. Serrano[1,3*]

[1]Thermochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra 3, Móstoles, Madrid, 28935, Spain; [2]Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 8, Prague, Czech Republic; [3]Chemical and Environmental Engineering Group, Rey Juan Carlos University, c/ Tulipán s/n, Móstoles, Madrid, 28933, Spain

[*]david.serrano@imdea.org

Introduction. Zeolites with high accessibilty play a fundamental role during the catalytic pyrolysis of wastes/residues as they are formed by bulky molecules. In particular, the MFI structure is one of the most employed zeolites in this type of reactions due to their unique combination of molecular sieve effect and acid properties. Likewise, the substitution of framework Al species for other heteroatoms allows tailoring the acid properties, thus varying the pyrolysis product distribution. In this work, we have synthesized highly accessible MFI zeolitic materials in the form of nanosponges (nSP) and nanosheets (nSH) with the incorporation of Al and Ga in the zeolitic framework. These materials have been tested as catalysts in the pyrolysis of oak wood and low density polyethylene (LDPE), which can be of interest for the productions of advanced fuels from biomass residues and plastic wastes.

Experimental/methodology. Aluminosilicate and gallosilicate in nanosponge and nanosheet samples (denoted as Al-MFI-nSP and Ga-MFI-nSP, Al-MFI-nSH, and Ga-MFI-nSH, respectively) were synthesized according to literature procedures[1,2]. The catalytic pyrolysis of LDPE was performed as described elsewere[3] at 350 °C for 2 h, with LDPE/catalyst mass ratios between 50 and 75. The oak wood pyrolysis set up is also decribed in a previous work[4], being operated with a catalyst to biomass ratio of 0.15, at 10 bar and temperatures of 500 / 450 °C for the thermal and catalytic zones, respectively.

Results and discussion. Both MFI-nSP and MFI-nSH samples display sharp variations, not only regarding morphology (Figure 1) and textural properties, but also in terms of acidic features. MFI-nSH samples exhibit a lower Bronsted/Lewis acid sites ratio than their analogous MFI-nSP samples. In addition, the presence of Ga in the zeolite framework, instead of Al atoms, enhances the Lewis acidity.

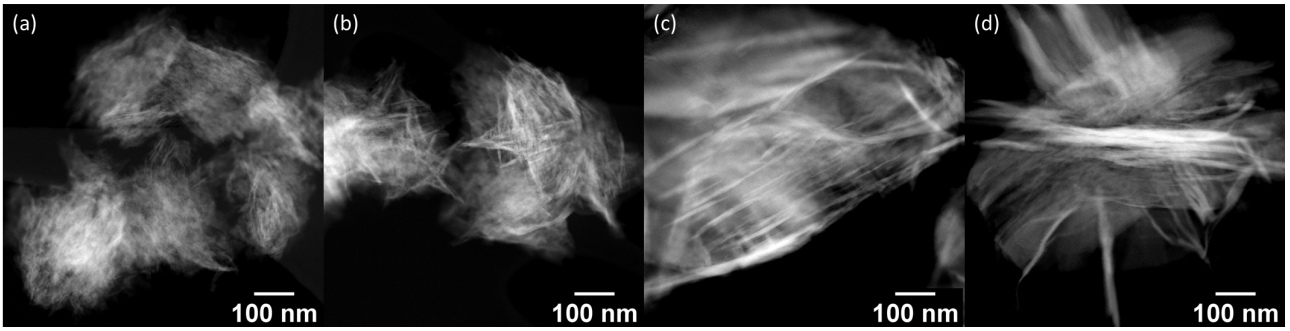

Figure 1. DF-STEM images of Al-MFI-nSP (a), Ga-MFI-nSP (b), Al-MFI-nSH (c), and Ga-MFI-nSH (d) samples.

These variations have a direct impact on the catalytic pyrolysis of LDPE and oak wood. Al/Ga-MFI-nSP display a superior activity than the Al/Ga-MFI-nSH for both LDPE and oak wood pyrolysis processes. In overall, an optimum combination of accessibility and a balanced Bronsted/Lewis acid concentration ratio has been found for the Ga-MFI-nSP sample, that leads to the best catalytic performance in the LDPE and oak wood pyrolysis.

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Chemical Recycling of thermoplastic Polymers with solid Catalysts

Marcus S. Lehnertz[1], Regina Palkovits[1*]

[1] *Institute for Technical and Macromolecular Chemistry at RWTH Aachen, Aachen, Germany*
[*] *palkovits@itmc.rwth-aachen.de*

Keywords: Chemical recycling, Heterogeneous catalysis, Biopolymers

Introduction. Being essential to our daily life, polymers have been produced in ever increasing amounts since the 1950's.[1] Especially within the last years, it became obvious that the development of recycling concepts for these indispensable substances could not keep up. Significant progress has been made towards mechanical recycling and the pyrolysis of polymers.[2] However, mechanical recycling cannot be repeated infinitively due to decreasing polymer quality over each cycle. Pyrolysis is usually carried out at high temperatures leading to an increased energy consumption. We therefore aim to implement solid catalysts in chemolytic recycling approaches to demonstrate the efficient conversion towards monomers and value-added products.

Experimental/methodology. The experimental setup features autoclaves in different volumes ranging from 5 to 975 ml. Majority of the catalysts is produced via wet impregnation and subsequent reduction under hydrogen atmosphere at elevated temperatures. To investigate the underlying catalytic phenomena, extensive analysis has been carried out, including nitrogen physisoprtion, temperature programmed reduction (TPR), CO-pulse, X-ray photoelectron spectroscopy (XPS) and IR-spectroscopy. Product analysis is carried out via HPLC, NMR, GC and GC-MS.

Results and discussion. The substrate scope covers bio-polyesters with rising markets such as polyhydroxy butyrate (PHB) and polylactic acid (PLA)[3-4] as well as established polymers, e.g. Nylon-66 and Poly(bisphenol A)carbonate (PC). It is demonstrated that pressures as low as 1 bar hydrogen are sufficient to activate the Ru-based catalyst. The required reaction temperature correlates with the melting point of the respective polymer, ranging from 160°C for PLA up to 250°C for Nylon-66. Water can often be used as a sustainable solvent, although methanol or dioxane are applied in special cases, e.g. for Nylon-66 and PC, respectively.[5] Due to their leading role for the reaction, a variety of supports for the Ru-based catalysts have been tested for their suitability, ranging from carbon to spinels and ceria. The performance of cerium oxide, either as a full catalyst or support material, stood out. One successful example is the conversion from PHB to its monomer 3-hydroxybutyric acid (3-HBA) with a yield of 79% and butyric acid (21%) as the solely side product.[3] Among other reasons, the activity of the catalyst system consisting of 0.5 - 5 wt% Ru on ceria is found to originate from weak Brønsted acid sites analysed by Pyridine-IR. Finally, the system is tested for its practical applicability by using all investigated polymers as substrates in a one-pot recycling approach.[5]

Acknowledgments
We gratefully acknowledge funding by the Exploratory Research Space of RWTH Aachen University (ERS) in the Center for Polymer Recycling (C4PR). This work was performed as part of the Cluster of Excellence Fuel Science Center (EXC 2186, ID: 390919832) funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities.

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Catalytic removal of brominated flame retardants from plastic waste

E. Olkkonen[1*], P. Auvinen[1], V. Nissinen[1], K. Grönlund[1], M. Suvanto[1], J. Jänis[1], J. J. Saarinen[1]

[1]*University of Eastern Finland, Department of Chemistry, Joensuu, Finland*
[*]*eerika.olkkonen@uef.fi*

Keywords: catalytic debromination, plastic waste, supported metal catalyst

Introduction. Plastic waste is suggested as one of the geological indicators of the so-called Anthropocene era. The exponential growth of plastics use together with their ubiquitous nature has resulted in plastic waste being now present in most terrestrial and marine environments followed by near-permanent contamination and serious environmental challenges (1,2). Many plastics based consumer goods contain flame retardants that inhibit combustion and propagation of fire. These often halogenated chemicals have been listed as persistent organic pollutants (POPs), and their use in consumer products is regulated by the Stockholm Convention due to their possible toxicity to humans and the environment (3). However, concentrations of flame retardants have been studied mainly in natural waters in wastewater treatment plants with modest concentrations (4) whereas in plastic recycling it is pivotal to study debromination at much higher concentrations. Thus, specific pre-treatments for plastic waste material is needed for improved recycling process to remove halogenated additives. Here we show that supported transition metal catalysts can provide a potential pathway for debromination of waste plastic feedstocks.

Experimental/methodology. Here catalytic debromination of brominated flame retardants was studied by using supported transition metal catalysts. Supported metal catalysts were prepared by strong electrostatic adsorption method (SEA) and studied in moderate conditions for debromination of tetrabromobisphenol A (TBBPA) in an organic solvent. Hydrodebromination reactions were carried out in a teflon sealed autoclave reactor under hydrogen atmosphere (210°C, 80 bar H_2). The initial bromine content of the solvent was set to 2 500 ppm. The debromination products were analyzed by using GC-FID, GC-MS (Bruker, DE) and 500 MHz NMR (JEOL, JP). Organic solvents were used for a higher initial flame retardant concentrations without diffusion problems that are relevant when dealing with recycled plastic waste streams.

Results and discussion. In this study we confirmed that supported transition metal catalysts have activity in reducing bromine content and converting TBBPA into less brominated compounds. Propagation of debromination was examined by GC-MS and NMR. Our experiments revealed that well dispersed Ni/TiO_2 catalysts prepared by SEA method were active in removing bromine from brominated flame retardants under reductive atmosphere in laboratory scale. According to our experiments, economically feasible catalytic debromination of plastic waste streams can be realized, especially by using Ni/TiO_2 catalyst prepared by SEA method. Such transition metal catalysts make it possible to lower the bromine content in recycled plastic waste to reach the bromine levels set by EU regulation. The findings of this study can be used to further develop new, environmentally more viable plastic recycling processes.

Acknowledgments
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Hydrogenolysis vs. Pyrolysis to Convert Polyethylene into Naphtha-like Products using Ni-Based Catalysts to Close the Gap in Circular Economy of Polyolefins

G. Celik[1*], A.C. Aydogdu[1], A. Süerkan[2], B. Erkmen[2], A. Ezdesir[2]
[1] *Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey*
[2] *SOCAR Turkey R&D and Innovation Inc., Product Development Department, Izmir, Turkey*
[*] *gcelik@metu.edu.tr*

Introduction. Plastic pollution has become a serious issue that is causing a threat to the environment and human health without proper recycling management [1]. Several technologies have been studied to convert plastic wastes into value-added products like fuel oil, diesel oil, and gasoline, with significant drawbacks such as high energy consumption and the production of lower-value-added compounds with poor quality [2,3]. The conversion of polyolefins to naphtha like compounds is of particular importance because naphtha can be used in commercial steam crackers to produce olefins, and subsequently virgin polyolefins, closing the gap in circularity of polyolefins. Herein, we investigate (i) whether naphtha-like liquid products can be obtained with pyrolysis (PYR) or hydrogenolysis (HYD) at high efficiency and (ii) performance of Ni-based catalysts as a replacement to their precious-metal containing counterparts.

Experimental/methodology. Ni-based catalysts were synthesized and reduced prior to use under H_2 at 700 °C. Catalytic activity experiments were performed in a Parr reactor at 20 bar and at a temperature range of 300-400 °C. Virgin PE (M_n=1700 Da & M_w=4000 Da) was used as a feedstock. Experiments were first performed to determine the conditions at which yield of liquid products was the highest. The liquid product was first distilled to obtain a liquid fraction having a boiling point less than 210 °C and analyzed using GC-MS as well as PIONA method to obtain n-paraffins, iso-paraffins, olefins, napthenes, and aromatics. Fresh and used catalysts were characterized by Scanning electron microscope (SEM), Brunauer-Emmett-Teller (BET), X-ray photoelectron diffraction (XRD), energy dispersive X-ray analysis (EDX), desorption of CO with diffuse reflectance infrared Fourier transforms spectroscopy (DRIFTS), and DRIFTS of adsorbed pyridine to gain knowledge about physical and chemical properties of the catalysts.

Results and discussion. The 1st part of the investigations focused on whether naphtha-like compounds can be obtained by PYR. Chromatography as well as chemical and physicals tests pointed out that liquid products obtained by PYR (yellow and orange liquids in Fig1) exhibit distinct differences than naphtha (colorless liquids in Fig1) and cannot be used as a feedstock for steam crackers. The 2nd part of the investigations focused HYD and PYR performance of catalysts. The activity testing on HYD of PE to produce linear saturated alkanes was performed with Ni-Cat_1 and Ni-Cat_2 under reaction conditions of $g_{feedstock}/g_{catalyst}$=3, 400 ºC, 20 bar H_2 and 5 h. It is found that the obtained distillates ranged from C_5-C_{12} as a colorless liquid containing mostly saturates *(*linear and cyclic alkanes) (Table 1). The thermal cracking of PE by Ni-Cat_1 and Ni-Cat_2 was yielded in 92% and 94% saturated compounds with a negligible amount of olefin and aromatics after distillation. When the reduced catalysts (Ni-Cat_{1R} and Ni-Cat_{2R}) were used, the yield of saturates was slightly decreased. Results indicate that the catalyst surface has a significant role in the selective formation of paraffinic naphtha-like high-valued chemicals through the deconstruction mechanism.

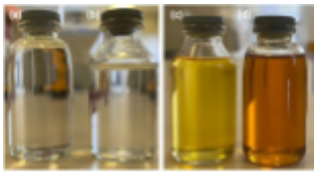

Fig 1. (a) Light naphtha, (b) Heavy naphtha, (c) and (d) Pyrolysis Oil.

Table 1. The Ni content of the catalysts and the product distribution of the HYD of PE *(*After distillation)*

Catalyst	Ni content (%)	Saturates* (w/w%)	Olefins* (w/w%)	Aromatics* (w/w%)
Ni-Cat_1	8.8	92	5	3
Ni-Cat_{1R}	n.d.	90	9	1
Ni-Cat_2	7.7	94	3	3
Ni-Cat_{2R}	n.d.	91	3	5

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Insights into the removal of antibiotics from water and wastewater by a laccase-mediator system

P.M. Álvarez[1*], A.M. Chávez[1,2], E. Rodríguez[1], I. Rodríguez[1], M. A. Figueredo[1,3]

[1] *Dept. Chemical Engineering and Chemical Physics, University of Extremadura, Badajoz, Spain*
[2] *Dept. Chemical Engineering, University of Porto, Porto, Portugal*
[3] *Dept. Environmental Technologies, University of Cadiz, Spain*
[*] *pmalvare@unex.es*

Keywords: antibiotics, laccase, syringaldehyde, water and wastewater treatment

Introduction. The increasing presence of different classes of antibiotics in water bodies generates great health and environmental concerns due to the microbial-resistance issue [1]. As a result, different methods are being investigated to remove antibiotics from wastewater. Some enzymes, including laccase, are receiving increasing attention as biocatalysts for this environmental application [2]. Because of its low redox potential (0.42-0.79 V), laccase has limited ability to oxidize organic compounds. However, in the presence of a specific redox-mediator (e.g., ABTS) laccase-driven degradation of antibiotics may be observed [3]. In this work, laccase from *Trametes versicolor* has been used for the removal of antibiotics belonging to different classes (e.g., tetracyclines, fluoroquinolones, sulfonamides, etc.) in the presence of redox mediators.

Experimental/methodology. Laccase from *Trametes versicolor* (activity ≥ 0.5 U/mg) was obtained from Sigma-Aldrich. ABTS and syringladehyde (SYR) were used as redox mediators. Experiments were carried out in ultrapure water (UP) and primary and secondary effluents from a municipal wastewater treatment plant (PE and SE, respectively) at pH ranged from 6.5 to 7.5. The following antibiotics were used: metronidazole, tetracycline (TET), oxytetracycline (OTET), sulfamethoxazole (SFX), sulfadimethoxine (SFM), ofloxacin, ciprofloxacin, flumequine and trimethoprim. Degradation of antibiotics was followed by HPLC-DAD. The ABTS assay was used for routine laccase activity determination.

Results and discussion. First, screnning experiments were carried out in UP to rank the antibiotics according to their enzymatic degradation rate. At pH 6.5 using ABTS as mediator, TET and OTET were completely degraded in less than 1 h while more than 90% SFM and 70% SFX were removed in 10 h (see Fig.1). The rest of the antibiotics tested were less prone to enzymatic biodegradation. SYR was demonstrated as an effective redox mediator for SFX degradation. The presence of organic matter in SE inhibited the enzymatic degradation of SFX to some extent and cause some enzyme deactivation. Also, simulataneous microbial (i.e., activated sludge) – enzymatic (laccase) biodegradation of SFX in PE was investigated.

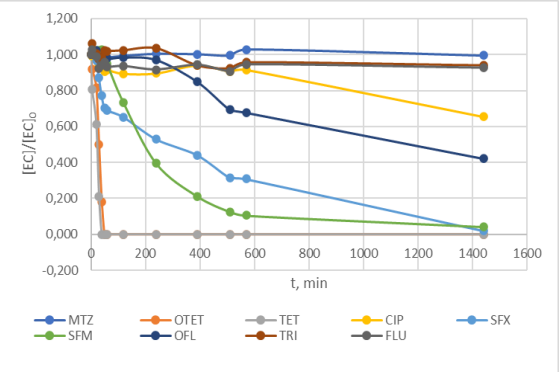

Fig.1. Laccase-mediated degradation of antibiotics. T=25ºC; pH=6.5; [Laccase]=100 mgL^{-1}; [ABTS]=0.036 mM; [EC]$_0$=0.5 mgL^{-1}

Acknowledgments
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Utilisation of in situ Generated H_2O_2 for Greywater Remediation

B. Bayntun[1*], T. Richards[1], R. J. Lewis[1] and G. J. Hutchings[1]

[1]*Max Planck–Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK.*
[*]*BayntunBH@Cardiff.ac.uk*

Keywords: Hydrogen peroxide, greywater remediation, bimetallic catalysts.

Introduction. Water sustainability is one of the most important challenges of the 21st century. Loss of water depletes energy reserves and undermines ecosystem health and human water security[1]. Current remediation of wastewater is heavily reliant on chlorination. One major downside to this method is the accumulation of toxic chemical residues in potable water. Hydrogen peroxide (H_2O_2) has the potential to replace chlorine-containing compounds for water remediation. It has a broad spectrum of bactericidal activity and water is the only by-product of its use, avoiding the by-products associated with chlorination. Commercial H_2O_2 has drawbacks, including the need to store large volumes of highly concentrated H_2O_2 on site and the need to remove propriety stabilizing agents prior to use. The in-situ production of H_2O_2 from H_2 and O_2 would avoid the drawbacks associated with the use of commercial H_2O_2 and allow for the decentralised treatment of greywater on a local level.

Experimental/methodology. A series of 1 wt% AuPd/TiO_2 catalysts was prepared by an excess-chloride co-impregnation procedure[2]**.** Catalyst testing was conducted in a continuous fixed-bed reactor to evaluate performance towards H_2O_2 synthesis and the remediation of model greywater.

Results and discussion. A synergistic effect was observed upon the alloying Au and Pd, leading to enhanced H_2O_2 productivity compared to the monometallic catalysts (Figure 1, left). The optimal 0.5%Au-0.5%Pd/TiO_2 catalyst displayed exceptionally high biocidal efficacy achieving an 8.1 $\log_{10}$ reduction (i.e. 99.999999%) in *E. coli* at a contact time of 1 minute, which was 10^7 times more effective than using an equivalent amount of preformed H_2O_2 and 10^8 times more effective than chlorination under equivalent conditions (Figure 1, right). EPR spectroscopy revealed the alloying of Au and Pd was essential in the production of several reactive oxygen species, which subsequently were responsible for the observed bactericidal efficacy.

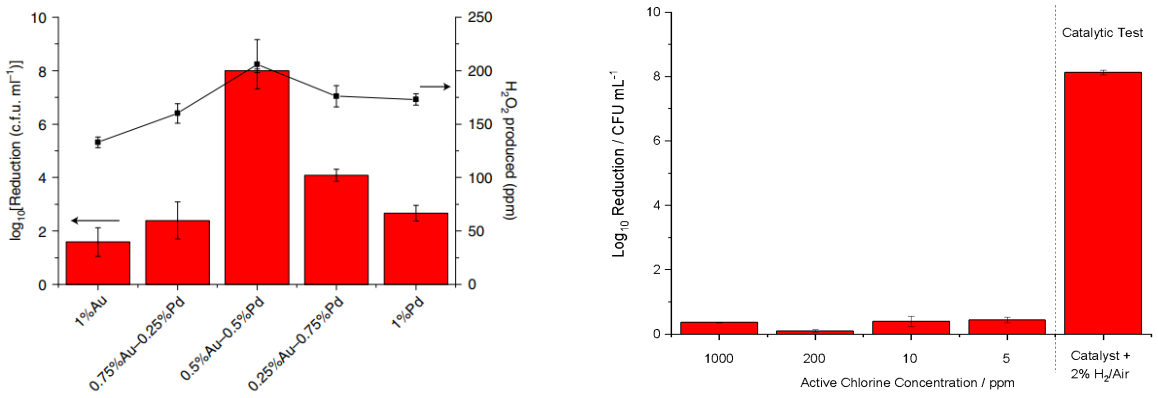

Figure 1. Left: Biocidal efficacy and H_2O_2 productivity of the 1% AuPd/TiO_2 catalyst series under flow conditions. Right: Biocidal efficacy of the optimal 0.5Au-0.5%Pd/TiO_2 catalyst compared to aqueous NaOCl under flow conditions.

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Heterogeneously SnPd-catalysed Nitrate and Nitrite Reduction in Aqueous Solution

J. Betting[1], L. Lefferts[1], J. A. Faria[1*]

[1]*Catalytic Processes and Materials – University of Twente, Enschede, The Netherlands*
[*]*j.a.fariaalbanese@utwente.nl*

Keywords: Bimetallic Catalysis, Multiphase Catalysis, Environmental Catalysis

Introduction: The development of a zero-emission ship engine system can reduce substantially the emissions generated from freight transport. This is very attractive in liquified natural gas (LNG) powered ships as the captured CO_2 can be converted back to methane using green hydrogen, enabling the circular use of carbon-based fuels. Unfortunately, the combustion of LNG emits a so-called "methane slip" as well as NO_x gases. To capture all the emissions, methane can be catalytically oxidized to CO_2 and the NO_x emissions can be scrubbed into liquid phase resulting in a nitrate and nitrite containing solution.[1] Converting these oxidized nitrogen species back to N_2 is key to prevent the disposal of these waters into the harbors as the high concentration of nitrates and nitrites will promote eutrophication of the water bodies and aquifers near the area.

Experimental/methodology: While monometallic catalysts suffice for the reduction of nitrites, bimetallic catalysts such as Pd-Sn, Pd-Cu or Pd-In are required for nitrate conversion (Figure 1).[2] For their reactivity, not only the metal combination but also the microscopic arrangements of the active sites are of importance. Therefore, bimetallic Pd-Sn catalysts are synthesized *via* sequential wet impregnation and controlled surface deposition resulting in random Sn-Pd or defined Sn-Pd structures, respectively. The catalysts are characterized and applied in rigorous reaction kinetic studies of nitrate and nitrate reduction.

Results and discussion: The comparison of differently synthesized bimetallic catalysts allows to establish fundamentally relevant property-chemistry-performance relationships and helps to establish the optimal catalyst formulation. In combination with detailed reaction kinetics mechanistic insights can be obtained and modelling of reactors for nitrate and nitrite reduction on ship is feasible.

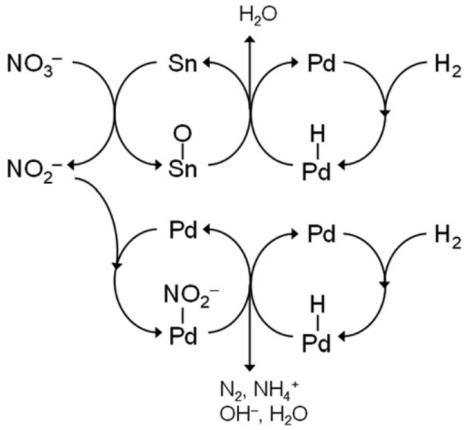

Figure 1: Reaction network of NO_x reduction showing the reduction of nitrate to nitrite by oxidation of tin to tin(II) oxide and subsequent tin regeneration by hydrogen spill-over. Nitrite is then reduced to nitrogen and ammonia as undesired side product.[3]

Acknowledgments
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Recycling of end-of-life long-chain polyamides via an ammonolytic hydrogenation process

R. Coeck[1*], A. De Bruyne[1], D. De Vos[1]

[1]*cMACS, Katholieke Universiteit Leuven, Leuven, Belgium*
[*]*robin.coeck@kuleuven.be*

Keywords: Nylon, polyamides, ammonolysis, hydrogenation, heterogeneous catalysis, polymer recycling

Introduction.

Polyamides (PAs) are important engineering plastics that find their use in a wide variety of applications as a result of their high stability. While PA6 and PA66 are often used for more general purposes (e.g. carpet), long-chain polyamides (LCPAs) are more expensive with better mechanical properties and are therefore mainly used in specialized niche applications (e.g. water pumps). Polyamides' high stability and durability are obstacles when dealing with end-of-life PA waste. Typically, one can deal with plastic waste via either landfilling, waste-to-energy (WtE) or recycling. Landfill is no longer acceptable; and for high value plastics it would be highly inefficient to burn the material and generate some electricity in the process (WtE), while continuing to produce virgin plastic from a mostly crude oil based feedstock.[1] This is particularly the case for nitrogen containing plastics such as polyamides, which in addition to typical greenhouse gases (i.e. CO_2), also release NO_x gasses. Although recycling is clearly the best option, efficient recycling methods are limited. Here, a new chemocatalytic ammonolysis process for LCPAs was developed, which can operate under relatively mild conditions and uses cyclopentyl methyl ether (CPME) as a green solvent.

Experimental/methodology.

Reactions were performed in a 25 mL pressure Parr batch reactor. In a typical reaction, the reactor is filled with a substrate containing 1 mmol secondary amide bonds, Nb_2O_5 catalyst (0.10 g of catalyst), RuWOx-catalyst (2 mol% Ru), undecane (20 µL) and CPME (10 mL). Then, the reactor is pressurized with 6 bar NH_3 and 50 bar H_2, and heated to 200°C. After reaction, the mixture is analyzed via H-NMR and GC(-MS).

Results and discussion.

The ammonolysis of *N*-hexylhexanamide, a model component for polyamides, was initially investigated. Niobium oxides (Nb_2O_5 and $Nb_2O_5.nH_2O$) were found to be effective heterogeneous catalysts. After a reaction time of 5 hours, a conversion of 36% was achieved with Nb_2O_5. Further kinetic experiments suggested that the ammonolysis reaches an equilibrium conversion (i.e. 45%) after 24 hours. Aside from the ammonolysis, niobium oxides also catalyzed the dehydration of primary amides. In a second stage, the ammonolysis was coupled to a hydrogenation process to convert the generated primary amides to primary amines. This resulted in a bicatalytic ammonolytic hydrogenation process with Nb_2O_5 and $RuWO_x/MgAl_2O_4$ as the corresponding catalysts. Actual industrial plastic samples (i.e. PA 10.10, PA 11 and PA 12) were completely depolymerized, leading to α,ω-diamines. The process was proven to be robust against common impurities (e.g. plasticizers, antioxidants, other plastic contaminations and fillers). However, any sulfur-containing compounds must be removed in order to maximize the lifespan of the Ru-catalyst.

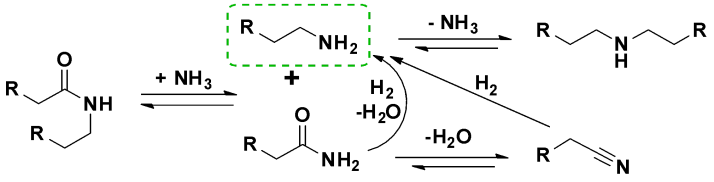

Figure 1. Ammonolytic hydrogenation of secondary amides to amines

Acknowledgments

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Production of low-chlorine oil through catalytic pyrolysis of solid recovered fuels (SRF) over ZSM-5, Beta and USY zeolites

J. Cueto[1], G. Pérez[1], M. Paniagua[2], G. Morales[2], J. A. Melero[2], D. P. Serrano[1,2]*

[1]*Thermochemical Processes Unit, IMDEA Energy Institute, Móstoles, Spain*

[2]*Chemical and Environmental Engineering Group, Rey Juan Carlos University, Móstoles, Spain*

[*]*david.serrano@imdea.org*

Introduction. Municipal solid waste production has increased considerably during the last decades. It is expected that this quantity will rise by up to 70 % in 2050 [1]. The current management policies are focused on prevention, reduction and mechanical recycling. However, not all the wastes can be recycled, so other uses must be found to prevent their accumulation in landfills. In this context, these wastes suppose a valuable source to produce solid recovered fuels (SRF), which consist of highly calorific fractions such as plastics, textiles, wood, and elastomers [2]. Among the available waste-to-energy or waste-to-chemicals technologies, pyrolysis has received an increasing interest due to its great flexibility and relatively simple operation. However, the use of SRF as feedstock for pyrolysis has been scarcely studied. Considering the heterogeneity of this raw material, the presence of high amounts of chlorine in its matrix may suppose an important limitation when it comes to feeding the final oil into a traditional refinery scheme. Consequently, the oil dehalogenation is one of the most determinant aspects to be understood. This work investigates the performance of various zeolites (ZSM-5, Beta and USY) in SRF catalytic pyrolysis in terms of dechlorination of the so-produced oil.

Experimental/methodology. SRF provided by 'Reciclados Palancia Belcaire' (Spain) has been pretreated by washing with milli-Q water and thermal heating at 300°C under N_2 flow. After this previous step, thermal and catalytic pyrolysis was carried out in an *ex-situ* set up passing an ascendant nitrogen stream. Temperatures of the thermal and catalytic zones were set at 550 and 400°C, respectively. 0.5 zeolite / SRF was used as mass ratio and the zeolites employed for catalytic runs were: n-ZSM-5 (Si/Al=42, Clariant), Beta (Si/Al=15, Clariant) and USY (Si/Al=40, Zeolyst).

Results and discussion. The main products of SRF catalytic pyrolysis are gaseous and liquid organic fractions, whereas in the thermal reaction waxes are mainly produced (Figure 1a), followed by a carbonaceous residue (char) and an aqueous phase. Interestingly, the gases are rich in light olefins, whereas the oil possesses a high content of aromatic hydrocarbons (with high differences between the zeolites tested: 87 and 47-48% for ZSM-5 and BETA-USY, respectively), which opens the way for their application not only in the production of fuels but also for raw chemicals. Other important finding is that chlorine is accumulated mainly in the char and aqueous phase fractions, thus leading to an oil with a relatively small Cl content (20 ppm in the oil for BETA).

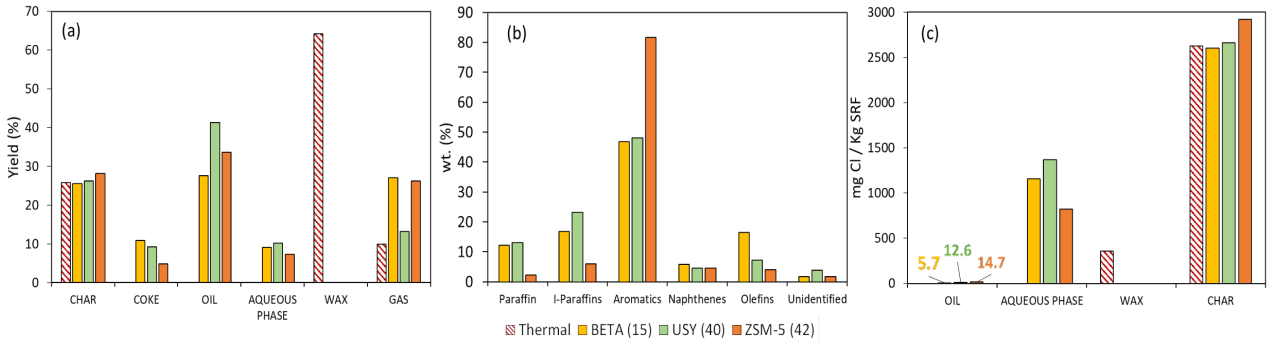

Figure 1. Fraction yields (a), oil composition (b) and chlorine distribution (c) in the SRF pyrolysis.

Acknowledgments

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Systemic expansion of territorial circular ecosystems for end-of-life foam

T.G.W. Engels[1*], P.J. Deus[1¥], H.J. Heeres[1¤]

[1]*University of Groningen, Groningen, Netherlands*
[*]t.g.w.engels@rug.nl
[¥]*p.j.deuss@rug.nl*
[¤]*h.j.heeres@rug.nl*

Keywords: Polyurethane, pyrolysis, catalysis, downstreaming

Abstract
Over the years, an increase of focus has been observed in the recycling of polyurethane (PUR) due to changes in regulation & environmental issues. The increase of landfill costs and decrease of space has forced more awareness in alternative recycling methods for polyurethane. [1] substantial research has concluded in three recycling and recovering methods that are economically and environmental accepted nowadays. 20% Mechanical processing (only postproduction waste), [1,2] 50% landfilling (combined postconsumer and postproduction waste), [3] and 30% is processed via thermal degradation (hydrogenation, pyrolysis, or gasification). [4] However, an efficient method to retrieve the starting material from end of life waste (EOL) is still desired.

For this reason, the Circular foam project has been started which is a collaboration between 23 parties within the EU with the polymer company Covestro as the leading organization. The project aims to design a downstream process for the conversion of EOL polyurethane found in refrigirators into raw material. which can be used to produce new polyurethane, resulting in a circular economy. Two approaches that have been considered are chemical and thermal decomposition. This work specifically focusses on thermal decomposition.

Pyrolysis has found it's way into industry via the recyling of biomass [5] and various plastics (PET, PE, PVC, PP, PS, PE, and Mix). [4] Pyrolysis is a process based on thermal decomposition. Long polymer chains are converted into smaller fragments at elevated temperature (350 – 900^{0}C) under anaerobic conditions (e.g. N_2 atmosphere). The resulting oil, gas and ash is of great value for industry. [4] Since pyrolysis has shown it potential by succesfully recycle various plastics and feedstocks, it has been chosen as the pathway to convert EOL PUR into virgin oil. Currently, the parameters of interest are temperature and choice of catalyst.

A general catalyst screening has been conducted to determine which type of catalyst is suitable for the depolymerization of PUR. A total of 10 different catalysts have been considered such as zeolites, clays, alumina's, and oxides e.g. H ZSM-5/zeolite HY, bentonite, various alumina oxide's and calcium oxide respectively. Positive results were observed with the use of alumina's and oxide's since significant amounts of desired products were observed.

As continuation of the project, an extended screening was conducted with analogs of the alumina or oxide based catalysts. However, no direct correlation between parameters of interest and formation of desired compounds was observed. For this reason Future work will revolve around analysis of various catalyst to verify which parameters have a significant influence on the formation of the desired products (e.g. particle size, BET, Brønsted/lewis acid sites etc.) In addition, model compounds will be synthesized and pyrolyzed in present of various catalysts to support the parameters of interest. These parameters will be investigated to a further extent.

Acknowledgments

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The Oxidative Degradation of Phenol *via in situ* H_2O_2 Synthesis using Pd-supported Fe-modified ZSM-5 Catalysts

L. J. Fisher[1*], A. Santos[1], R. J. Lewis[1], D. J. Morgan[1,2], T. E. Davies[1], E. Hampton[3], P. Gaskin[3] and G. J. Hutchings[1]

[1]*Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK.*

[*]*FisherL4@Cardiff.ac.uk*

Keywords: Hydrogen peroxide**,** oxidative degradation, bifunctional Pd/Fe-ZSM-5 catalysts.

Introduction: The contamination of water bodies with pollutants from petrochemical, pharmaceutical and agricultural waste streams is a rising dilemma and induces risk to human and aquatic life[1]. Conventional techniques for water treatment are highly reliant on chlorination, however, there are concerns regarding the accumulation of toxic chemical residues, as well as increased energy demand associated with the use of alternative stoichiometric oxidants[2]. The oxidative degradation of organic pollutants *via* the *in-situ* synthesis of H_2O_2 has the prospect to substitute chlorine-containing compounds for water treatment due to diminishing the health and environmental implications while contributing increased activity in contrast to previous procedures to water treatment.

Experimental/Methodology: A series of PdFe-ZSM-5 catalysts were prepared *via* an excess chloride impregnation procedure. Catalyst testing was conducted in a Parr Instruments stainless steel autoclave reactor to investigate the efficacy towards the degradation of phenol and enhance improvements towards catalyst stability over previously studied materials.

Results and Discussion: Time-on-line studies reveal that generally catalytic performance towards H_2O_2 formation is not detrimentally affected by the addition of Fe and despite the introduction of Fe, the degradation of phenol was favoured. The greatest rate of phenol conversion was attained by 0.5 wt% Pd/3 wt% Fe-ZSM-5 (70 %) over 2 h in comparison to 0.5 wt% Pd/0.5 wt% Fe-ZSM-5 (45 %). XPS analysis revealed the surface speciation of the monometallic Pd catalyst is comprised of a combination of both Pd^0 and Pd^{2+}. The inclusion of Fe generates a significant shift in Pd oxidation state with the quantity of Pd^0 escalating significantly. Thus, the increase in H_2O_2 synthesis activity and phenol degradation activity of the Fe-containing catalysts can be assigned to the variation of Pd oxidation state.

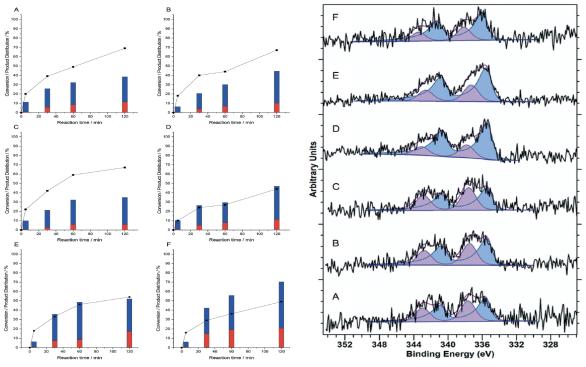

Figure 1. (**Left**) Comparison of the catalytic activity towards the oxidative degradation of phenol *via in situ* H_2O_2 synthesis as a function of reaction time over. (**A**) 0.5 wt% Pd/ZSM-5, (**B**) 0.5 wt% Pd/0.06 wt% Fe/ZSM-5, (**C**) 0.5 wt% Pd/0.125 wt% Fe-ZSM-5, (**D**) 0.5 wt% Pd/0.5 wt% Fe-ZSM-5, (**E**) 0.5 wt% Pd/1 wt% Fe-ZSM-5 and (**F**) 0.5 wt% Pd/3 wt% Fe-ZSM-5. Key: selectivity towards phenolic derivatives (red bar), selectivity towards organic acids (blue bar), H_2 conversion (black squares). (**Right**) Pd(3d) core-level spectra for (**A**), (**B**), (**C**), (**D**), (**E**) and (**F**). Key: Pd^0 (blue), Pd^{II} (purple).

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More information can be found at: A. Santos *et al*. *The Oxidative Degradation of Phenol via in situ H_2O_2 Synthesis using Pd Supported Fe-modified ZSM-5 Catalysts*. Catal. Sci. Technol., **2022**, *12*, 2943-2953. DOI: 10.1039/d2cy00283c.

Wet peroxide oxidation of paracetamol: overview of typical catalysts

F. F. Roman[1,2], A. Santos Silva[1,2], A. P. F. da Silva[1,2], J. L. Diaz de Tuesta[3], M. Kalmakhanova[4], D. Snow[5], H. T. Gomes[1,2*]

[1]*Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Portugal*
[2]*Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Portugal*
[3]*Department of Chemical and Environmental Technology, ESCET, Rey Juan Carlos University, Spain*
[4]*Department of Chemistry and Chemical Technology, M.Kh. Dulaty Taraz Regional University, Kazakhstan*
[5]*School of Natural Resources and Nebraska Water Center, part of the Robert B. Daugherty Water for Food Global Institute, University of Nebraska, Lincoln, USA*
[*]*htgomes@ipb.pt*

Introduction. Intense population growth has significantly impacted drinking water quality, resulting in release and accumulation of contaminants of emerging concern (CECs) in water bodies. Pollution by CECs is likely to increase, requiring the development of practical efficient treatment technologies. Catalytic wet peroxide oxidation (CWPO) is a technology that has demonstrated some advantages, allowing complete degradation of several CECs. This work compares the efficiency of several catalysts (clays, carbon-based and hybrid materials) in the CWPO of paracetamol (PCM), a model pharmaceutical compound.

Experimental/methodology. The synthesis of pillared clay (PCLAY), carbon nanotubes (CNT@PP) and hybrid carbon-coated magnetic nanoparticles (CoFe@C) are reported elsewhere [1-3]. CWPO reactions were conducted considering the following conditions: $[PCM]_0$ = 100 mg L^{-1}, $[H_2O_2]_0$ = 474 mg L^{-1}, pH_0 = 3.5, T = 80 °C, $c_{catalyst}$ = 2.5 g L^{-1}, 24 h. PCM and H_2O_2 were followed by HPLC and UV-Vis, respectively, as described in previous works [1].

Results and discussion. The results are summarised in Fig. 1. The removal of PCM in the presence of CoFe@C is much faster than CNT@PP and PCLAY (Fig. 1,a), especially if excluding the effect of adsorption (Fig 1,c). The consumption of H_2O_2 follows the order CoFe@C > PCLAY > CNT@PP (Fig. 1,b). The leaching of iron is higher for PCLAY, followed by CoFe@C and CNT@PP (Fig. 1,c). Thus, CNT@PP allows for a similar degradation of PCM to PCLAY while resulting in lower leaching. The hybrid material (CoFe@C), on the other hand, shows great potential by resulting in a faster PCM degradation and lower iron leaching.

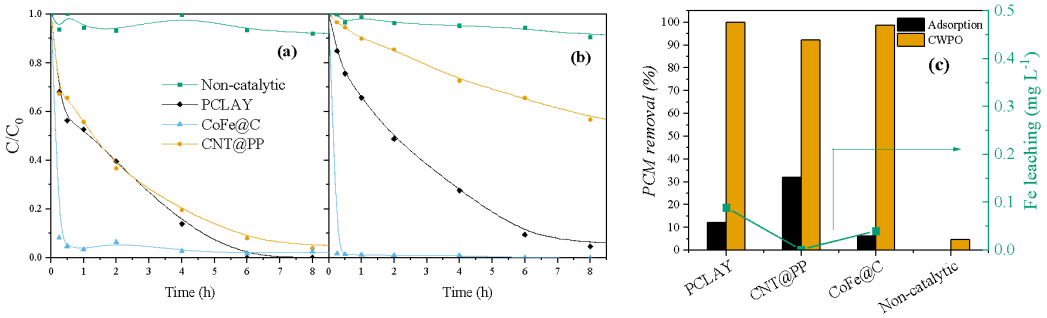

Fig. 1. Normalized concentration of (a) PCM and (b) H_2O_2, and (c) comparison between adsorption, CWPO, and iron leaching.

Acknowledgments

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Influence of bicarbonate, other anions and carbon dioxide in the activity of Pd-Cu catalysts for nitrate reduction in drinking water

D.T. González[1], J.A. Baeza, L. Calvo, M.A. Gilarranz
[1]*Universidad Autónoma de Madrid, Madrid, Spain.*
[*]*dydia.gonzalez@uam.es*

Introduction. Catalytic reduction is an interesting removal technique as it is able to convert nitrate into harmless gaseous N_2 using a reducing agent such as H_2, without generating any secondary waste. However, it is also necessary to make sure that harmful intermediates as NO_2^- and NH_4^+ are avoided since they are also regulated for EU. Therefore, it is key to control the selectivity in the reaction. The effect of ions in natural waters have been investigated by several authors, showing catalyst deactivation, and favouring NH_4^+ formation. In addition, various studies have shown that anions, especially HCO_3^-, have a more negative effect on the catalytic activity. Therefore, in this work the effect of salts on NO_3^- reduction using a Pd-Cu catalyst supported on carbon black has been investigated, with a focus on the reaction mechanism and fate of HCO_3^-.

Experimental/methodology. The effect of different ions usually present in drinking water (Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and HCO_3^-) has been studied. For this purpose, two types of water were tested: synthetic water (SW) and commercial drinking water (DW) spiked with NO_3^- ($[NO_3^-]_0$ =100 mg/L). The experiments were carried out in a glass reactor jacketed at 25 °C and atmospheric pressure using a Pd-Cu (2:1) catalyst, 5 wt%, supported on carbon black (ENS350). During the nitrate reduction cycles H_2 (1 NmL/min) and CO_2 (50 NmL/min) were continuously bubbled. For the specific study of the effect of HCO_3^-, a serie of assays were performed in which 100 mg/L HCO_3^- was added at zero time reaction.

Results and discussion. The results of ions effect in the water showed that in the presence of low concentrations, no noticeable variations were seen in the catalytic activity. However, when the tested water contained high concentrations, mainly of anions (55.6 mg/L Cl^-, 52.1 SO_4^{2-}), NO_3^- conversion may be affected, obtaining a final conversion of 82 % and a NH_4^+ selectivity higher than 20 %. Previous studies related to the ions effect on the NO_3^- catalytic reduction have attributed the decrease in NO_3^- catalytic activity to competition for adsorption on the active sites [1]. In addition, a significant effect was observed in the catalytic activity when the HCO_3^- ion was present in the tested water (39.8 mg/L Cl^-, 52.8 SO_4^{2-}, 298 mg/L HCO_3^-), obtaining a final conversion of 57.2 %. Thus, a specific study about HCO_3^- effect was carried out, comparing reactions with Milli-Q water in absence and presence of this anion. Total conversion was obtained in both reactions due to the high activity of the catalyst. However, the time necessary for total conversion in the HCO_3^- absence was 60 min, increasing up 120 min when HCO_3^- was present. In addition, low HCO_2^- concentrations were found in these reactions, which suggests that a HCO_3^- reduction was taking place during NO_3^- catalytic reduction. Studies related to HCO_3^- reduction suggest a mechanism similar to NO_3^- nitrate reduction [2], so there would be a competition for adsorption in the active sites and availability of H_2 for the reduction to HCO_2^- and NO_2^-, respectively.

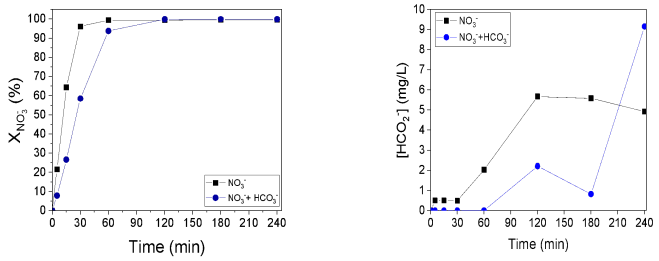

Figure 1. (a) Effect of HCO_3^- on NO_3^- conversion, (b) Formation of HCO_2^- vs time reaction on nitrate reduction with Pd-Cu/ENS350.

Acknowledgments
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Continuous catalytic integrated treatment for organic and inorganic species abatement

A. Sofia G. G. Santos [1,2]*, A. Rita. L. Ribeiro[1,2], João Restivo [1,2], Carla A. Orge [1,2], M. Fernando R. Pereira [1,2], O. Salomé G. P. Soares [1,2]

[1] *Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

[2] *ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

[*] *Corresponding Author's E-mail address: up201303231@fe.up.pt*

Keywords: Catalytic ozonation; Catalytic reduction; Macrostructured catalysts; Integrated catalytic treatment.

Introduction. Heterogeneous catalysis, applied for water treatment, has been widely studied to remove several organic and inorganic contaminants occuring in water [1]. Although different reaction conditions and catalysts are necessary to remove both types of pollutants, this methodology appears as a simpler, efficient, and economical alternative to perform definitive remediation of different classes of contaminants [1,2]. Bromate (BrO_3^-) is a carcinogenic compound of great environmental concern, is a typical by-product resulting from ozonation of bromide-containing waters or from oxidation of brominated organic compounds; it is classified as a possible human carcinogen; and is regulated at a maximum of 10 µg/L in drinking water [3]. The present work aims to develop an integrated continuous catalytic system, for the simultaneous removal of organic and inorganic species in water, using adequate macrostructured carbon catalysts. The system consists on the serial application of catalytic ozonation for the degradation of water contaminated with brominated organic compounds, followed by a catalytic reduction process for BrO_3^- conversion into Br^-.

Experimental/methodology. Macrostructured catalysts were synthesized using a washcoating methodology (CNT coated macrostructured catalysts and Pd-Cu bimetallic macrostructured catalysts supported on CNT:TiO_2) [4]. Catalytic experiments were performed in a custom-made experimental set-up. Brominated organic pollutants (Bromophenol Blue, Tetrabromobisphenol A, and 2,4,6-Tribromophenol) were studied as model contaminants susceptible to generate BrO_3^-, after ozonation treatment (C_0=1 mg L^{-1} of each pollutant), that would be afterwards converted into Br^- during the second process. Organic species concentration was followed using liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS); BrO_3^- quantification was performed using a HPLC-LC20-AI with post column reaction.

Results and discussion. The integrated treatment system was applied for the complete treatment of water contaminated with brominated organic pollutants. The absence of catalyst in the oxidation system allowed the full degradation of the organic species with a higher formation of BrO_3^-, and the absence of catalysts in the hydrogenation column did not promote BrO_3^- conversion; also, the use of a catalysts during ozonation treatment plays a key-role on the decrease in the amount of BrO_3^- formed after oxidation of the organic species. The results obtained allowed to conclude that, after the application of the catalytic ozonation treatment, the organic pollutants were fully removed from the water leading to the formation of high BrO_3^- concentrations (concentration above the limit allowed by law). When directly forwarded to catalytic reduction treatment, it was possible to decrease BrO_3^- concentration present in the water for values very close to its maximum legal limit in water (10 µg L^{-1}, conversion of around 86 %). The catalysts proved to remain stable and active (without metal phase leaching) during long reaction periods.

Acknowledgments

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Development of one-pot synthesized Ti-SBA-15 catalyst for oxidative desulfurization for upgrading of advanced biodiesel

A. Guntida[1], J. Apariccio[2], F. Maugé[1], K. Thomas[1*]

[1] *Université de Caen Normandie, CNRS, ENSICAEN, Laboratoire Catalyse et Spectrochimie (LCS), 14000 Caen, France*

[2] *DIELIX - Sarpi Veolia, 727 Rte du Hazay, 78520 Limay, France*

[*] *Corresponding Author's e-mail address: karine.thomas@ensicaen.fr*

Keywords: oxidative desulfurization, dibenzothiophene, DBT, mesoporous silica, SBA-15, titanium

Introduction.

To replace fossil-based fuel, biodiesel production from waste cooking oil is environmentally friendly and gives renewable energy with lower pollution. However, biodiesel contains high amount of impurity, such as sulfur, and needs to be purified before using in a vehicle engine [1]. Oxidative desulfurization (ODS) is a promising method to remove sulfur compounds. Oxidation of organosulfur compounds leads to the formation of their sulfoxides/sulfones, which are highly polar and thus can be easily removed by polar solvents [2]. Titanium-containing mesoporous materials have attracted attention because of larger access to the active site and the presence of coordinately unsaturated tetrahedral titanium able to interact with the primary oxidant, leading to excellent catalytic activity [3]. In this work, a one-pot incorporation of titanium into SBA-15 framework was synthesized and compared to a conventional impregnated catalyst. The ODS of dibenzothiophene (DBT) as a model sulfur-containing compound was investigated, and their surface properties were related to the ODS activity. Eventually, the one-pot synthesized catalyst showed outstanding catalytic activity in the ODS system.

Experimental/methodology.

SBA-15 sample was prepared using an aqueous solution of pluronic P123 triblock copolymer and hydrochloric acid. Tetraethoxysilane (TEOS) was used as the silicon source. One-pot synthesized Ti-SBA-15 catalysts with various titanium loading were prepared by co-condensation of TEOS and titanium acetylacetonate or titanium butoxide. For the incipient wetness impregnated catalyst, titanium acetylacetonate in ethanoic solution was dropped slowly into SBA-15. Finally, the samples were calcined at 550 °C for 5 hours. The ODS of DBT was conducted at 80 °C for 2 hours in the presence of hydrogen peroxide (H_2O_2/DBT = 4 molar ratio).

Results and discussion.

Titanium containing SBA-15 catalysts provided well-defined hysteresis loop of type H1 associated with capillary condensation and desorption in open-ended cylindrical mesopores and there were large surface area (830 - 880 m²/g) and big pore size (4.5 - 5.2 nm). The Lewis acidity of the catalyst prepared by the titanium acetylacetonate precursor was higher than that of the catalyst prepared by the titanium butoxide precursor revealed by in situ IR of pyridine adsorption. ^{29}Si NMR spectroscopy gave an evidence of titanium inserted into silica framework for the one-pot synthesized catalyst. These data show the better dispersion of titanium and the presence of active Ti^{4+} tetrahedral sites through Si-O-Ti bonds in the one-pot preparation.

At the same titanium loading, the novel titanium incorporated SBA-15 catalyst by one-pot synthesis showed largely superior ODS activity (100 %) compared to the conventional impregnated catalyst (51 %). Moreover, the ODS activity of the one-pot synthesized catalyst rapidly reached 100 % within 15 minutes in case of Si/Ti molar ratio 10 and 20. In this work, a novel one-pot synthesized Ti-SBA-15 catalyst was developed with high activity in the oxidative desulfurization of DBT, which should also exhibit high efficiency in removing sulfur-containing compounds in biodiesel derived from waste cooking oil.

Acknowledgments

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Full Catalytic Dehalogenation of Brominated Flame retardants

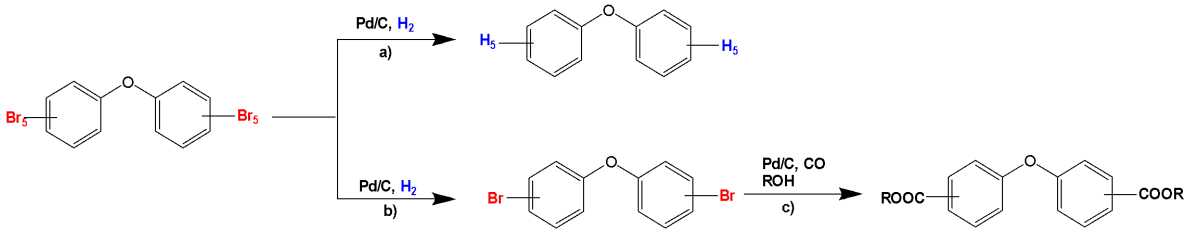
Gj. Hulaj, S.Windels, B. Krasniqi, D. De Vos*

Centre for Membrane separations, Adsorption, Catalysis and Spectroscopy – KU Leuven, Leuven, Belgium
*dirk.devos@kuleuven.be

Introduction

Brominated flame retardants belong to a large group of organohalogen chemicals, which are used in a variety of polymers such as high-impact polystyrene and epoxy resins, which are then used in commercial products such as computers, electronics and electrical equipment, textiles, and furniture foam [1]–[2]. It is important to note that some of them are now in use, some are banned, and others under assessment [3]. As these compounds are nearly impervious to degradation and highly environmentally persistent with deleterious effects on human health, there is a real incentive to develop technologies to rid the environment of such deleterious substances. The best current method is to debrominate them fully via pyrolysis, hydrothermal treatment, or catalytic pyrolysis. However, this leads to a very low-value fraction which is at best suitable to be used as fuel [4]. Ultimately the compounds are burned or incinerated. Here we explore different strategies to catalytically detoxify or upcycle these BFRs.

Regarding debromination, we developed a catalytic method to convert BFRs into valuable products. This catalytic method includes two pathways (see scheme 1.) for revalorization of BFRs: full debromination via hydrogenolysis reaction using Pd/C, and partial debromination via hydrogenolysis in combination with deep dehalogenation via carbonylative debromination. The resulting oligo-carboxylic acids or esters are easily recovered and revalorized, e.g. in resins.



Scheme 1. a) Full hydrogenolysis of BFRs; b) Partial hydrogenolysis and c) model reaction: catalytic conversion of dibromodiphenyl ether to diester.

Results and discussion

After the completion of the reaction, high yields of bromine-free valuable products were obtained under mild conditions using Pd/C as a catalyst (Table 1). Regarding the second pathway, DecaBDE was chosen as a model reactant, in which after the partial hydrogenolysis reaction, a yield of about 35% of dibromodiphenyl ether was obtained. The latter was then used as a model for the carbonylative debromination reaction using Pd/C as a catalyst. About 80% yield of dimethoxycarbonyl diphenyl ether was obtained, which is a valuable product for the production of polyesters.

Table 1. Full hydrogenolysis of BFRs for 6h using Pd/C (5 wt%) 5 mol% , 2,6 - Lutidine as a solvent and base

Entry	Substrate	T (^{0}C)	p(H_2) bar	Product	Yield [%]
1	Decabromodiphenyl ether	75	5	Diphenyl ether	89
2	Decabromodiphenyl ethane	75	5	Dibenzyl	94
3	Tetrabromobisphenol A	100	10	Bisphenol A	95
4	1,2-bis(2,4,6-tribromophenoxy)ethane	75	5	1,2-diphenoxyethane	98
5	Hexabromocyclododecane	100	10	Cyclododecane	83

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Plastic Waste Recycling via Zeolite-based Hydrocracking

L. Chen[1*], N. Michailidou[1], L. Radloff[1], S. Winiesdorffer[1], M. Geske[1], M. Al-Naji[1], M. Bender[2] and F. Rosowski [1,2]

[1]*BasCat – UniCat BASF Joint Lab, TU Berlin, Berlin, Germany*
[2]*BASF SE, Catalysis Research, Ludwigshafen, Germany*
[*]*lunhan.chen@tu-berlin.de*

Introduction. Only a small fraction of around 12% of plastic waste is recycled world-wide, with mechanical recycling as the main established method [1]. However, mechanical recycling is limited to pure polymers and the polymer quality is degrading with each cycle. New technologies for chemical recycling of plastics are on the rise, in which pyrolysis is the most investigated and developed method [1]. In pyrolysis, chemical bonds are thermally cracked, resulting in a wide range of hydrocarbons and high amount of coking [2]. Depending on the obtained pyrolysis oil quality, a hydrogenation step as after-treatment is required to purify the product fraction by removal of heteroatoms. Therefore, catalytic hydrogenative cracking could be an alternative to pyrolysis in order to obtain a valuable liquid product fraction of saturated hydrocarbons within one procedure step [2].

Experimental/methodology. The typical experiments are carried out in a batch reactor (300 mL) from Parr instruments at temperatures between 250 – 340 °C, 60 bar of H_2 pressure, 700 rpm and 2 – 15h of reaction time. The hydrogenative fragmentation of Polyolefins into a range of hydrocarbons in gas (C1 – C4), liquid (C5 – C21) and wax (C>21) products is studied. Gas phase products are analyzed with GC coupled with TCD. The liquid and wax composition are separately identified and quantified with GC-MS and GC-FID. Parent zeolites, with different Si/Al molar ratio, and metal loaded zeolites were investigated in the reactions mentioned above.

Results and discussion. Among different tested reaction temperatures, experiments at 300 °C with selected zeolites resulted in a high liquid product fraction. The yield of gas and liquid fractions are shown in Figure 1, obtained after the conversion of LLDPE over HZSM-5 and H-BEA of similar Si/Al ratios of 15 and 12.5, respectively, and at reaction times between 2 and 15h. Zeolite HZSM-5 was reported to pre-dominantly produce gas products which was also observed in this work [2-3]. Despite the similar Si/Al ratios, LLDPE conversion with H-BEA resulted in a significant higher amount of liquid yield (42% after 4h). With longer reaction times, the liquid yield is decreased as longer hydrocarbons are cracked into shorter, volatile alkanes [4]. The liquid product composition validated the fragmentation of LLDPE to alkanes, via cracking and H-transfer on acid sites, as well as further aromatization to aromatic products. It is noteworthy to mention that, with longer reaction times from 2h to 15h, the alkane yield is decreased from 49% (2h) to 14% (15h) alkanes, whereas aromatics increased from 37% (2h) to 67% (15h). In summary, the acid sites of investigated parent zeolites alone are active enough to convert LLDPE into alkane and aromatic products, which makes zeolite-based supports a promising choice for the hydrogenative cracking of polymers.

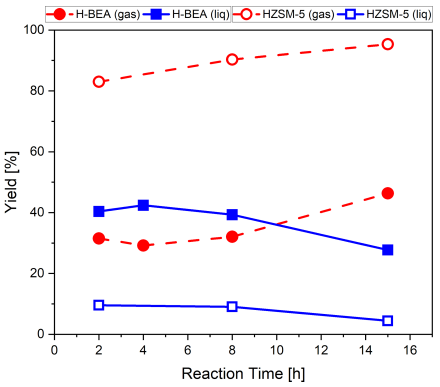

Figure SEQ Figure * ARABIC 1: Gas and liquid yields from LLDPE with parent zeolites at 300 °C, 60 bar H_2 and 700 rpm, from 2 – 15h.

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Three-stage pyrolysis-catalysis of polyolefins over MFI and Ni-MFI catalysts for BTEX and syngas production

Amer Inayat[1*], Katerina Klemencova[1], Alexandra Inayat[2], Pavel Lestinsky[1]

[1]*Institute of Environmental Technology, CEET, VSB -Technical University of Ostrava, Ostrava, Czech Republic*
[2]*Institute of Chemical Reaction Engineering, Friedrich-Alexander University (FAU), Erlangen, Germany*
[*]*amer.inayat@vsb.cz*

Keywords: Pyrolysis, chemical recycling, zeolite catalysts, Thermo-chemical processes

Introduction. The exponential growth of plastic wastes represents serious threats to both terrestrial and marine ecosystems. The conventional waste treatment methods (mechanical recycling and incineration) are not able to cope with the waste generation rate (especially of impure/contaminated plastics) and ever stricter environmental regulations on CO_2 emissions and required recycling rates. Here, chemical recycling is considered as an important alternative to mechanical treatment and incineration of plastic wastes. It allows for the transformation of waste plastics into basic chemical substances which can be used as secondary feedstocks in chemical and petrochemical industries [1]. Chemical recycling via thermo-catalytic pyrolysis is an attractive approach to transform plastic wastes into useful chemicals, and in this regard, zeolites and zeolite-based materials are among the versatile catalytic materials for the thermo-catalytic treatment of plastics [2,3,4]. In our work [4] on chemical recycling of plastics, we presented a systematic study on the thermo-catalytic pyrolysis of polyolefins over MFI (HZSM-5) zeolite catalysts (in one and two-stage processes) to produce aromatics and light olefins. In continuation of this recent study, the present work deals with pyrolysis-catalysis of polyolefins with an aim to produce BTEX rich pyrolysis oil and syngas.

Experimental. For the pyrolysis-catalysis of polyolefins, a three-stage experimental setup was employed. In the first stage, pyrolysis vapors were produced by thermal (non-catalytic) treatment of polyolefins. In the second stage, thermo-catalytic conversion of the pyrolysis vapors over MFI (HZSM-5) zeolite catalyst was carried out to obtain pyrolysis oil and gas. After the second stage, the pyrolysis oil produced was separated from the pyrolysis gas. The pyrolysis gas was then mixed with Ar and CO_2 and fed to the third stage reactor for catalytic dry reforming over Ni loaded MFI (silicalite-1) zeolite catalyst for syngas production. In the second stage, commercially available HZSM-5 zeolite was used as catalyst, whereas for the third stage Ni/Silicalite-1 catalyst was prepared. All catalyst materials were characterized by XRD, NH_3-TPD, H_2-TPR, SEM, and N_2 physisorption. The influence of catalyst properties, as well as the operating conditions on the product distribution was investigated.

Results and discussion. The results obtained from the preliminary tests confirmed that in the second stage, the composition of pyrolysis oil (BTEX content) and gas (C_1-C_4 alkanes and C_2-C_4 olefins mainly) can be tuned by varying the reactor temperature as well as the acidity of the HZSM-5 catalyst. Furthermore, in the third stage, 20%Ni/silicalite-1 showed appreciable conversions of pyrolysis gas and CO_2 to syngas at 700 °C. A detailed and systematic study on the influence of catalyst properties, reactor temperature at different stages and GHSV (in the third stage) on the product distribution is underway and the results will be presented.

Acknowledgments
Experimental results were accomplished by using Large Research Infrastructure –Energy Waste Recovery and Gas Treatment supported by the Ministry of Education, Youth and Sports of the Czech Republic under Project Number LM2023056.

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Enhanced Production and Control of Liquid Alkanes in the Hydrogenolysis of Polypropylene over Shaped Ru/CeO_2 Catalysts

Ajay Tomer[1], Mazharul M Islam[2], Mounib Bahri[3], Donald R Inns[1], Troy D Manning[1], John B Claridge[1], Nigel D Browning[3], C Richard A Catlow[2], Alberto Roldan[2], Alexandros P Katsoulidis[1], Matthew J Rosseinsky*[1]

[1] Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, UK. [2] Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, CF10 3AT, Cardiff, UK. [3] Albert Crewe Centre for Electron Microscopy, University of Liverpool, Liverpool L69 3GL, UK.

**Corresponding author: m.j.rosseinsky@liverpool.ac.uk*

Introduction: The large-scale production and consumption of polyolefins such as polypropylene (PP) is leading to the generation of significant amounts of environmentally damaging plastic waste, with the majority being buried as landfill [1]. A promising route to chemically recycle plastic waste is the catalytic hydrogenolysis process to generate high yields of valuable liquid alkanes through selective internal C-C bond cleavage [2]. Given this, we have developed highly active shaped Ru/CeO_2 catalysts (nanocube and nanorod) for the hydrogenolysis of various pristine and post-consumer polypropylene to liquid alkanes. Furthermore, the chain length of the produced liquids could be controlled via alteration of the reaction conditions. This control allows for tuning of the liquid reaction product dependent on the intended application.

Experimental: Shaped CeO_2 (nanocube and nanorods) were synthesised by a hydrothermal method according to literature [3]. Non-shaped CeO_2 was purchased from Sigma Aldrich. The catalysts (Ru/CeO_2) were prepared using an incipient wetness method using $Ru(NO)(NO_3)_3$ and calcined at 500 °C. Catalysts were denoted: NR – nanorod, NC – nanocube, SA – Sigma-Aldrich. Catalysts were pre-reduced at 300 °C for 2 h prior to testing. Hydrogenolysis reactions were carried out using a Parr reactor with 2 g polymer and 0.1 g catalyst. The reaction was carried out at various temperatures (180-250 °C), metal loadings (0.5-5 wt.% Ru), H_2 pressures (10-30 bar), and reaction times (8-60 h). Analysis of gas fraction was conducted using GC-FID and the liquid fraction was analysed by GPC. Catalyst characterisation was performed on fresh catalysts to identify structure-activity relationships and include XRD, BET, CO chemisorption, ICP-OES, TEM, and H_2-TPR.

***Table 1**. Catalytic performance of 2Ru/CeO_2-(SA/NR/NC) in the hydrogenolysis of isotactic polypropylene-12 kDa.*

	Y_{solid}(%)	Y_{liquid}(%)	Y_{gas}(%)	Liquid M_w (Da)	PDI
Ru/CeO_2-SA	47	43	10	5451	2.41
Ru/CeO_2-NR	28	70	10	1924	2.35
Ru/CeO_2-NC	5	68	27	984	1.5

Results and discussion: The 2 wt.% Ru/CeO_2 catalysts were observed to have well-dispersed Ru species by CO chemisorption, TEM and XRD, with the shaped catalysts showing enhanced Ru dispersion (NR = 100% and NC = 72%) when compared to the non-shaped (SA = 23%). H_2-TPR also showed different Ru speciation for the shaped catalysts and enhanced H-spillover onto the support. This enhancement of the metal-support interaction and smaller cluster size led to increased activity for the shaped catalysts when compared to the non-shaped. Optimisation of the reaction conditions allowed for control of the product yields and liquid product chain length, as shown in Figure 1 for different reaction times. Table 1 shows the catalytic results for the hydrogenolysis of PP (Mw 12 kDa) under optimised conditions (220 °C, 30 bar H_2, 500 RPM, 16 h), with the NC catalyst which exhibited the highest activity with the shortest liquid hydrocarbons (984 Da) with

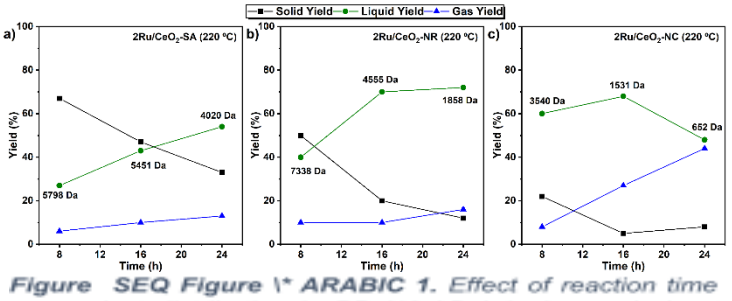

***Figure SEQ Figure * ARABIC 1**. Effect of reaction time on product distribution in PP (12 kDa) hydrogenolysis at 220 °C for 2 wt.% Ru supported a) CeO_2-SA b) CeO_2-NR, c) CeO_2-NC catalysts.*

the smallest polydispersity index (1.5). In addition, post-consumer PP products such as file sheets, fragrance cases, and centrifuge tubes were successfully depolymerised over the shaped catalysts.

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Magnetic $MnFe_2O_4$/PILCs for removal of methylene blue by catalytic wet peroxide oxidation

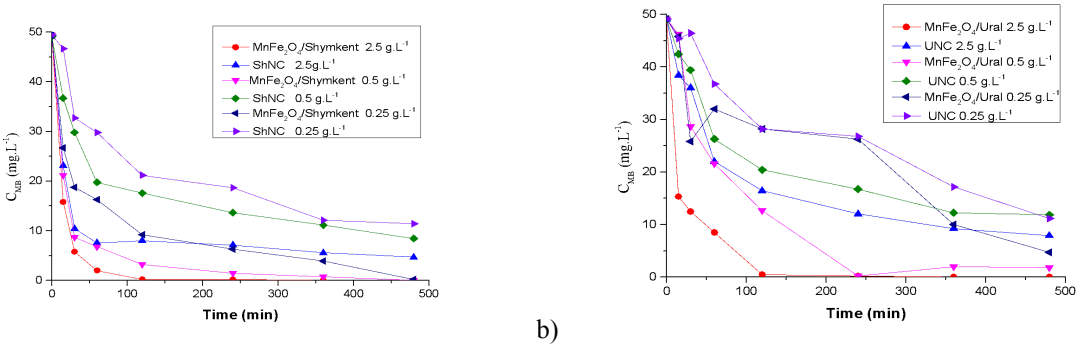
Zh. A. Baimuratova[1,2,3], A.S. Silva[1,2], J.L. Diaz de Tuesta[1,2,4], H.T. Gomes[1,2], M.S. Kalmakhanova[3,*]

[1]*Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Portugal*
[2]*Laboratório para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Portugal*
[3]*Department of Chemistry and Chemical Technology, M.Kh. Dulaty Taraz Regional University, Kazakhstan*
[4]*Department of Chemical and Environmental Technology, ESCET, Rey Juan Carlos University, Móstoles, Spain*
[*]*marjanseitovna@mail.ru*

Introduction. Catalytic wet peroxide oxidation (CWPO) is one efficient technology that uses proper catalysts for the decomposition of H_2O_2 into hydroxyl radicals, responsible for oxidizing organic pollutants. In this work, a new method for synthesizing magnetic pillared clays (MPILCs) was developed for further application in the elimination of dyes from aqueous solutions by CWPO. The MPILCs were prepared from natural clays found in large deposits of Kazakhstan (ShNC and UNC, from Shymkent and Ural deposits, respectively) by intercalation of iron and manganese cations in the space between the layers of clay silicates upon hydrolysis with NaOH. The activity of the MPILCs as catalysts for CWPO were tested and evaluated in the decomposition of the dye methylene blue (MB).

Experimental/methodology. The MPILCs were synthesized by adapting the procedure presented elsewhere [1]. The co-precipitation of Mn(II) and Fe(III) occurred upon the addition of NaOH solution (5 mol L^{-1}) until pH 10 was obtained. The solution was stirred for 30 minutes on a magnetic stirrer and heated to 100°C. Then, the solids were separated from the water, dried in an oven at 105°C for 2 h, and further calcined at 400 °C for 3 h in a muffle furnace, resulting in $MnFe_2O_4$/Shymkent and $MnFe_2O_4$/Ural, depending on the natural clay used as precursor. The CWPO experiments were conducted considering the following conditions: $C_{MB,0}$= 50 mg L^{-1}, catalyst dose = 0.5-2.5 g L^{-1}, T = 348 K.

Results and discussion. The results are shown in Fig. 1. Increasing the dose of MPILCs, the active centers available for catalyst-H_2O_2-MB interactions increase, achieving higher MB removal (Fig. 1a, b). Comparing the results, it is observed that the removal of MB in the presence of $MnFe_2O_4$/Shymkent (Fig. 1a) occurs much faster than with $MnFe_2O_4$/Ural (Fig. 1b). Natural clays exhibit low catalytic activity compared to the developed $MnFe_2O_4$/PILC catalysts. The catalysts also show good resistance to the leaching of metal particles into solution, being thus concluded that $MnFe_2O_4$/PILCs demonstrate great potential for further application in treatment of real complex wastewater.



a) b)

Fig. 1. Effect of catalyst dose on the removal of methylene blue by CWPO with the a) Shymkent natural clay (ShNC) and $MnFe_2O_4$/Shymkent, and b) Ural natural clay (UNC) and $MnFe_2O_4$/Ural, as a function of reaction time.

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Systematic screening of conventional and hierarchical zeolites for the catalytic conversion of end-of-life tyre pyrolysis vapours to aromatics

S.D. Stefanidis[1], S.A. Karakoulia[1], E. Pachatouridou[1], E. Heracleous[1,2], A.A. Lappas[1,*]

[1] *Chemical Process and Energy Resources Institute, Centre for Research and Technology-Hellas, Thessaloniki 57001, Greece*

[2] *Department of Science & Technology, International Hellenic University, Thessaloniki 57001, Greece*

[*] *angel@cperi.certh.gr*

Keywords: Tyres, recycling, catalytic pyrolysis, zeolites, aromatics

Introduction. Over 1 billion new tyres are sold globally every year, and a roughly equal number of them enter the pool of end-of-life tires (ELTs). The tyre recycling methods used nowadays do not produce materials that can be reused by the tyre industry, while ~50% of the EU's ELTs are not recycled and are instead exported to other countries. This study is part of the EU project BlackCycle, which aims to develop a technology for the recycling of ELTs into raw materials that can be used for the production of new tyres. Via pyrolysis, ELTs can be converted into pyrolysis oil, solid and gas products. Highly aromatic pyrolysis oils can be used as feedstock for the production of virgin carbon black, which is a major component in the manufacturing of tyres. In this work, conventional and hierarchical zeolites with variable silica-to-alumina ratios (SAR) and catalyst-to-feed (C/F) ratios were screened for the catalytic conversion of ELT pyrolysis vapours towards aromatic compounds.

Experimental/methodology. The ELT feedstock was provided by Aliapur S.A., and was described as "granules of multi-brand truck tyres 1-3 mm". The conventional zeolites used were Y zeolites with SAR 5 and 30, a ZSM 5 zeolite with SAR 80 and a Beta zeolite with SAR 25, all purchased from Zeolyst. Hierarchical Y and ZSM-5 zeolites were used as well. The hierarchical Y was synthesised by desilication of the commercial Y SAR 30 (Y SAR 30 DS), while the hierarchical ZSM-5 was synthesised by desilication of the commercial ZSM-5 SAR 80 (ZSM-5 SAR 80 DS). The screening was carried out in a bench-scale fixed bed reactor using 2.8 g of ELT and
C/F ratios of 0.25, 0.5 and 1. Both the pyrolysis and the catalytic conversion temperatures were 500 °C.

Results and discussion. Upgrading the ELT pyrolysis vapours with any of the zeolites used resulted in a decreased yield of pyrolysis oil in favour of permanent gases and coke formed on the surface of the zeolites. However, this was accompanied by a significant increase in the aromaticity of the pyrolysis oils, as indicated by their increased C/H molar ratio (**Figure 1**). In the case of the Y zeolites, the Y SAR 5 resulted in the most modest increase of the C/H ratio, which indicated that its high density of acid sites was not favourable for the efficient conversion of the ELT vapours. On the other hand, the Y SAR 30 achieved significantly higher C/H ratios when compared to the Y SAR 5. The Beta SAR 25 achieved similar C/H ratios as the Y SAR 30, but with reduced pyrolysis oil yield. The ZSM-5 SAR 80 achieved a more moderate increase in the C/H ratio, accompanied by a moderate decrease in the pyrolysis oil yield. This was attributed to a lower activity of the ZSM-5 SAR 80, which in turn was attributed to the small pores of the ZSM-5 structure. Finally, the hierarchical zeolites Y SAR 30 DS and ZSM-5 SAR 80 DS exhibited higher activity and achieved the highest C/H ratios in the pyrolysis oils, while at the same time, they achieved a more moderate reduction of the pyrolysis oils yield compared to their conventional counterparts.

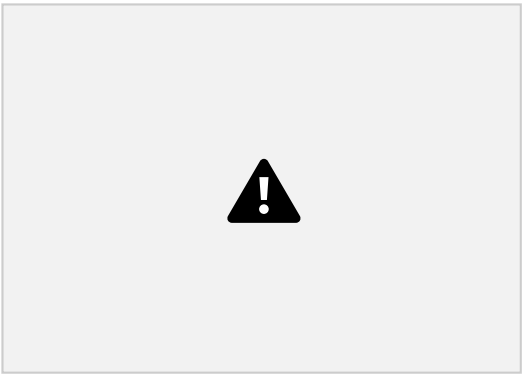

Figure 1. C/H molar ratio of the pyrolysis oils produced with the different catalysts vs. the pyrolysis oil yield.

Acknowledgements

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Decomposition of an azo dye by an advanced oxidation process using innovative surface-functionalised PAN fibre catalyst

M. Kocijan [1*], S. Rashid [2], K. Huddersman [2]

[1] *Department of Materials, Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Zagreb, Croatia*
[2] *Leicester School of Pharmacy, Faculty of Health and Life Sciences, De Montfort University, Leicester, United Kingdom*
[*] *martina.kocijan@fsb.hr*

Keywords: PAN, catalyst, azo-dye, advanced oxidation process

Introduction: Nowadays, accessible clean water and energy resources are among the highest priorities for sustainable economic growth and societal well-being. Water scarcity is an increasing problem globally making it imperative that wastewater is treated and reused in industrial processes, for irrigation and feeding livestock, thus saving potable water for drinking [1]. Emerging contaminants such as azo dyes and their transformation products have adverse impacts on human health and the environment. The textile industry is one of the fastest-growing industries daily. Dyeing wastewater accounts for around a quarter of the total industrial wastewater and has become a serious worldwide environmental issue because of low biodegradability and the high toxicity of their transformation products. Reactive orange 16 (RO16) is a reactive azo dye with a nitrogen-nitrogen (N=N) bond. The main challenge in the decolourization and degradation of azo dyes is the breakdown of azo bonds, leading to the removal of dye from water. Conventional wastewater methods such as adsorption, biological treatment, filtration, chemical treatment, and flocculation are not efficient in degrading the aromatic and heterocyclic structures of the dye molecules. Therefore, extensive efforts have been directed globally toward the development of suitable, efficient, and eco-friendly processes for the removal of persistent pollutants. Advanced oxidation processes (AOPs) have the potential to achieve complete mineralisation of pollutants from water. Currently, most AOPs are employed using hydrogen peroxide (H_2O_2), Fenton reactions, catalysts, ultraviolet (UV) light, and a combination of Fenton reactions with UV light (photo-Fenton), and catalysts with UV light (photocatalysts). Up till now, effective catalysts are produced in the form of a powder suspended in a model solution of pollutants but there has been difficulty in sustaining their immobilisation on suitable substrates. Many existing reactors use produced nanoparticles in the form of suspension where the separation and reuse of the catalyst are difficult to achieve with significant catalyst loss, efficiency, and cost-effectiveness of the process [2], [3].

Experimental/methodology: The presented study aims to investigate the removal of RO16 dye as a model of recalcitrant pollutants using the photo-Fenton process. The solid phase catalyst [4], a surface functionalised polyacrylonitrile (PAN) fibre comprising iron (III) was tested for a varied number of parameters (wavelength of light, hydrogen peroxide concentration, reusability of the catalyst, and the extent of leaching of the active site of the catalyst). The removal of RO-16 from the water was monitored by measuring the absorbance at 254 nm (removal of aromaticity) and 493 nm (decolourisation) by UV-Vis spectrophotometer.

Results and discussion: The obtained results of performed tests show the efficient removal rate of aromaticity of RO16 dye using the photo-Fenton process changing varied number of parameters. The results of reusability (after five consecutive cycles) show no deactivation of the catalyst occurred, which indicates its potential long-life span for its efficient working in the removal of contamination from water which is making it highly suitable for scale-up implementation.

Acknowledgments

M. Kocijan would like to thank British Scholarship Trust Foundation for the grant supporting this research at the De Montfort University, Leicester, UK.

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Direct Conversion of Glycerol into Glycidol in a Gas-Phase Packed-Bed Reactor over Caesium-Treated ZSM-5 Catalysts

Andrii Kostyniuk[1*], David Bajec[1], Blaž Likozar[1]

[1]*National Institute of Chemistry, Ljubljana, Slovenia*
[*]andrii.kostyniuk@ki.si

Keywords: HZSM-5, caesium nitrate, glycerol, dehydrative epoxidation, glycidol.

Introduction. Glycerol is the main byproduct in the biodiesel industry representing roughly 10% of the mass of the biodiesel produced, which led to a decrease in glycerol commercial price due to its high abundance on the world market. Glycerol valorisation can be carried out in a gas phase over heterogeneous catalysts, where acrolein, acrylic acid, dihydroxyacetone, hydroxyacetone, allyl alcohol, epichlorohydrin, lactic acid, 1,2-propanediol, 1,3-propanediol, ethanol and very recently glycidol are the most promising value-added products of this process [1,2]. Glycidol is an important product for industrial commercialization due to its many applications and its high profitability on the world market. For example: as a monomer and semi-product in the synthesis of surfactants, polyurethanes, polyamides, polycarbonates, polyesters, high-boiling polar solvents, lubricating oils, components for body care products, laundering detergents, disinfectants, etc. Our group has implemented recently [3] the "green" and one-step glycidol production from glycerol without H_2 in a gas-phase packed-bed continuous-flow reactor under atmospheric pressure.

Experimental/methodology. The synthesis of the caesium zeolite catalysts with SiO_2/Al_2O_3 = 30 and 1500 molar ratios was obtained by the wet impregnation method. The influence of Cs species incorporation into ZSM-5 zeolite on the acidity-basicity and its catalytic performance was elucidated. The structural, morphology, acidic, and basic properties of alkali-treated zeolite catalysts were systematically investigated by various analytical techniques such as ICP–MS, XRD, N_2 physisorption, STEM–EDX, SEM, pyridine-DRIFT, CO_2–TPD, NH_3–TPD, and TGA. The reaction was carried out in the laboratory Microactivity-Reference reactor (PID Eng&Tech). Typically, 0.5 g of the catalyst was placed in a packed-bed tubular reactor and stabilized with glass wool on both sides. The 10 wt% aqueous solution of glycerol was injected into the hot box with a 307 HPLC Piston Pump (Gilson Inc.). The carrier gas was N_2 (20 ml/min) and its flow was controlled by a mass flow controller. The hot box and reactor were kept at 140 °C and 350 °C, respectively.

Results and discussion. In this work, the catalysts evaluation results indicated that the 20wt%Cs/ZSM-5(1500) catalyst was the most effective in the direct glycerol conversion into glycidol via dehydrative epoxidation reaction with the participation of basic sites (Figure 1).

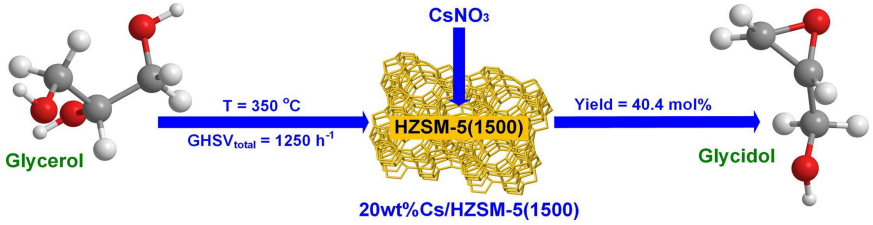

Figure 1. Catalytic dehydrative epoxidation of glycerol into glycidol.

This catalyst showed relatively high stability and selectivity, which was attributed to the presence of a suitable amount of basic sites and the strong $CsNO_3$/HZSM-5 support synergetic interaction. It was observed that Si species partly dissolved from the HZSM-5 framework. At the same time, the conversion of glycerol reduced from 86.3 mol% to 27.4 mol% within 3 h time-on-stream. On the other hand, the selectivity increased from 41.4 mol% to 64.3 mol% after 27 h. The highest achieved glycidol yield was 40.4 mol% with 10 wt.% glycerol in the feed at 350 °C reaction temperature and $GHSV_{total}$ = 1250 h^{-1}.

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Rare-earth metal oxides nano-dispersed onto ligno-humic-like support derived from sewage sludge for waste wates treatment

V. La Parola[1*], R.Comparelli[2], M.L. Curri[2,3], M. Dell'Edera[2,3], L. di Bitonto[4] C. Pastore[4], L. F. Liotta[1]

[1] Institute for NanoStructured Materials, National Council Research (ISMN-CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy; [2]CNR-IPCF, Istituto per i Processi Chimico-Fisici, S.S. Bari, c/o Dip. Chimica Via Orabona 4, 70126 Bari, Italy; [3]Università degli Studi di Bari Aldo Moro, Dip. Chimica, Via Orabona 4, 70126 Bari, Italy; [4]Institute of Water Research, National Council Research (IRSA-CNR), Via de Blasio 5, Bari, 70132. Italy;

Keywords: Ceria, Titania, LHLs, water remediation

Introduction. The performances of semiconductor photocatalysts, like titania or ceria, can be tuned by appropriately doping with heteroatoms, like noble metals, which significantly decrease the band gap to visible light range. Another strategy to improve semiconductor properties is the ligand-to metal charge transfer with aromatic compounds. [1] The use of naturally occurring aromatic, like lignocellulose recovered from specific biomasses, has recently been investigated for titania [2]. This work deals with the preparation of carbon-activated CeO_2 and TiO_2 as photocalysts for the removal of water contaminants. As source of aromatic dopants were used ligneo humic like compound (LHLs) obtained by sewage sludge treatments which lead to a double benefits, namely recovery of resources and containment of the final waste to be disposed of, in coherence with "circular economy" principles.

Experimental/methodology. Three LHLs were used for the synthesis of CeO_2-LHLs and TiO_2-LHLs composites: 1) commercial (comm), extracted by primary sludge (PS), and extracted by sewage scum (SS). The oxides were precipitated in presence of the LHLs with a weight ratio of 10 MeO_2 to 1 LHLs and 1 MeO_2 to 1 LHLs. The obtained materials were treated at 250°C in N_2 flow. The samples obtained, along with the corresponding oxides without LHLs, were characterized by BET, XRD, TGA under air flow, XPS, SEM and UV-vis. The degradation of methylene blue by standard procedure ISO 10678 (2010) will be used to evaluate the catalytic activity.

Results and discussion. The different LHLs used were able to modify the characteristic of the cerium and titanium oxides both in terms of morphologies and in terms of electronic properties. In Figure 1 the TGA and its derivative of the N2 treated samples are displayed. The profile of decomposition of the different LHLs interacting with TiO_2 is function of the nature of the ligneo humic compound used as carrier for titania growth.

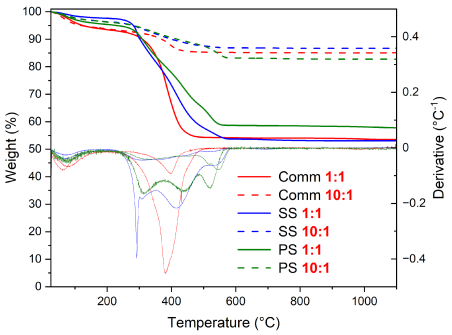

Figure 1. TGA and derivative of TiO_2 supported on humic acid: comm, SS and PS with ratio Ti/LHLs =1:1 or 10:1.

Acknowledgments

Progetto Wondercat- Progetti di ricerca @CNR (CUP B53C22000710001)

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Catalytic upgrading of waste plastic pyrolysis oil

V.-L. Yfanti[1], H. Zoupidis[1], A. Margellou[1], K. Triantafyllidis[1,2], A.A. Lemonidou[1,2]

[1]*Aristotle University of Thessaloniki, Thessaloniki, Greece*
[2]*Chemical Process and Energy Resources Institute, CERTH, Thessaloniki, Greece*
[*]*alemonidou@cheng.auth.gr*

Keywords: plastic wastes, pyrolysis oil, zeolites, circular economy

Introduction

Plastics have an important and growing role in our economy and daily lives, providing many benefits like food and drungs safety. However, their high production rate, short usage time, and poor waste management led to their ever-growing accumulation in nature. The latter along with plastic's non-biodegradable nature has caused serious negative effects on the environment and human health [1]. Considering the above issues, chemical recycling of plastic wastes, like pyrolysis, is one of the main sustainable alternatives to regenerate and reuse plastics, simultaneously contributing to a circular economy for plastics and to disposal waste volume reduction [2].

This study refers to ex-situ catalytic upgrading of mixed plastic wastes pyrolysis oil to a higher quality oil (with gasoline-like properties), suitable to be served as a feed to steam crackers already used in petrochemical industries, for further conversion to plastic monomers. Efforts are directed towards developing a selective and stable catalyst and process options, so as to avoid overcracking to gas products.

Experimental/methodology

The experiments of pyrolysis oil upgrading were performed in gas phase and in a fixed-bed reactor, using model compound (eicosane) as feed. The effect of the solvent on eicosane conversion was studied using octane and dodecane as solvents (15 wt% eicosane in octane or dodecane, 400 °C, W/F = 164 $g_{cat} \cdot h\ mol_{C20H42}^{-1}$) over a commercial SiO_2/Al_2O_3 catalyst (SAR=5.9, BET= 573 m^2/g).

Results and discussion.

In the presence of octane and dodecane as solvent, eicosane was converted by 52% and 35.5% respectively, mainly forming liquid products. Under the selected reaction conditions 60-70% of the products formed are in the range of C5-C15 with the rest being C1-C4 gases (mostly propylene and iso-butylene). Worthy to note that pure octane and dodecane showed negligible conversion, under the same conditions. Further characterization by TPO, TPD, BET of the used catalysts will be performed to determine coke deposits and adsorbants and to understand the reasons for the observed difference in eicosane's conversion and the loss of activity.

Except of the $SiO_2/A_{l2}O_3$ catalyst, preliminary tests using model compounds mixture as feed will also be conducted over microporous zeolites with tailored acidic characteristics. Moreover, in order to improve the catalytic performance (increase catalyst activity, isomerization and hydrogenation rate), metals like Ni, Cu, Mo are to be doped on the above catalysts. The effluent will be analysed and characterised with several methods (e.g. GC/FID, GC-MS, NMR, GPC). The best preforming catalysts in terms of activity and selectivity are going to be evaluated for the upgranding of the real plastic waste pyrolysis oil, both in batch and continous flow conditions, and they will be thoroughly characterized for coke deposits, halogen and metal poisoning. The preparation of the catalysts and their evaluation in the selective upgrading of plastic pyrolysis oil is in progress.

Acknowledgments

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The degradation of phenol via in situ H_2O_2 production over supported Pd-based catalysts

R. J. Li[1*], A. Santos[1], R. J. Lewis[1], D. J. Morgan[1], T. E. Davies[1], and G. J. Hutchings[1]

[1]*Max Planck–Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK.*
[*]*LiR58@Cardiff.ac.uk*

Keywords: In-situ H_2O_2 production, Pd-based catalysts, phenol degradation

Introduction. Hazardous and harmful organic compounds in industrial wastewater endanger public health and the natural environment.[1] To date, various chemical/biological treatment techniques have been widely developed for removing those contaminants (e.g. phenols). Among them, the hydrogen peroxide (H_2O_2)-based Fenton reaction has been considered a potential water treatment approach due to its superior efficiency and technical feasibility, by generating highly active radical and non-radical species (e.g. $HO^{\cdot}$, $O_2^{-\cdot}$, $^1O_2$) via the Fenton pathway for organic pollutants removal. However, using highly concentrated H_2O_2 pre-formed through the industrial anthraquinone oxidation (AO) process faces storage and transportation issues and environmental hazards.[2] Therefore, the strategy of in-situ H_2O_2 production directly from H_2 and O_2 avoids the above issues and promotes decentralized local water treatment using the in-situ Fenton pathway.

Experimental/methodology. A series of mono- and bi-metallic 1wt.% Pd-Fe/TiO_2 catalysts were prepared using an excess-chloride co-impregnation procedure.[3] Catalytic activity was conducted using a Parr Instruments stainless steel autoclave to evaluate the performance towards in-situ H_2O_2 synthesis and Phenol degradation.

Results and discussion. Enhanced catalytic activities toward phenol conversion were observed over bi-metallic 1wt.%Pd-Fe/TiO_2 catalysts, with the highest rate of phenol conversion (46%) achieved over a 2 h reaction using the optimal 0.25wt.% Pd–0.75wt.% Fe/TiO_2 formulation, almost four times more active than the Pd-only analogue. XPS analysis revealed that the introduction of Fe caused a clear shift in Pd speciation, towards Pd^{2+}, and simultaneously increased the amount of Fe^{2+} species in 1wt.%Pd-Fe/TiO_2 catalysts, which are responsible for generating reactive oxygen species (e.g. $^{\cdot}OH$) by activating H_2O_2 via Fenton pathway.

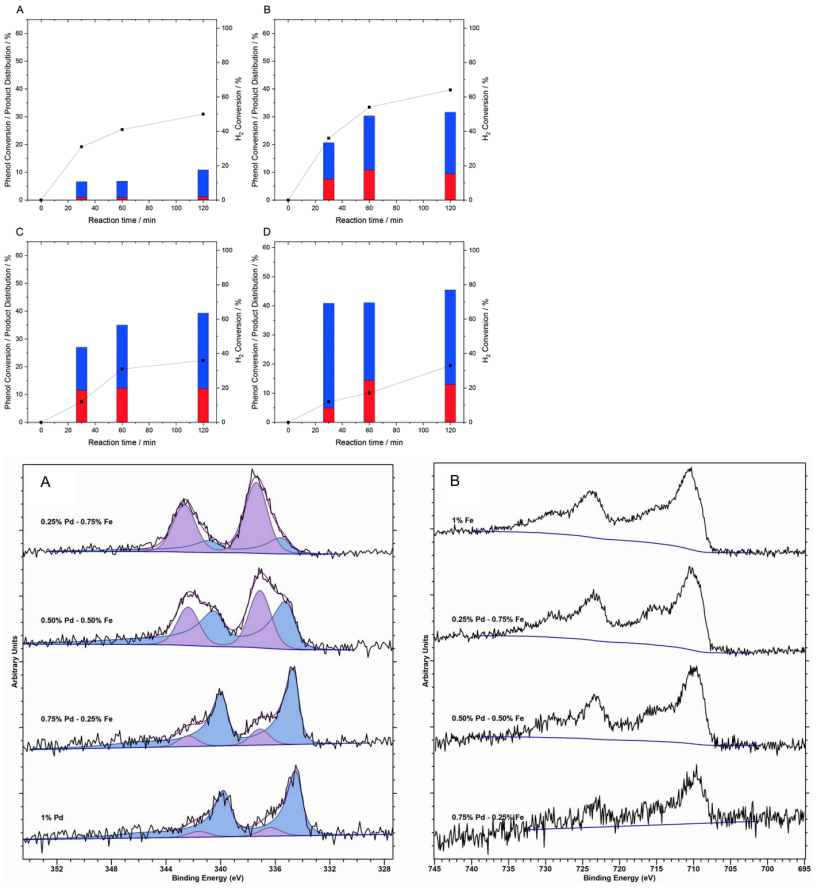

Figure 1. (Left) The catalytic activity of 1wt.% Pd-Fe/TiO_2 catalysts towards the oxidative degradation of phenol, via in situ H_2O_2 production. (A) 1wt.% Pd/TiO_2, (B) 0.75wt.% Pd–0.25wt.% Fe/TiO_2, (C) 0.5wt.% Pd–0.5wt.% Fe/TiO_2, and (D) 0.25wt.% Pd-0.75wt.% Fe/TiO_2. Key; selectivity towards phenolic derivatives (red bar), selectivity towards organic acids (blue bar), H2 conversion (black squares). (Right) XPS spectra of Pd(3d) (A) and Fe (2p) (B) regions for the as-prepared 1wt%PdFe/TiO_2 catalysts. Key: Metallic Pd (Blue) and Pd(II) Oxide (Purple).

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Non-thermal-plasma assisted degradation of perfluorooctanoic acid

J. Paul Guin[1,2*], N. Gurrin[1], D. Molloy[1], J.A. Sullivan[1*]

[1]*School of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland*
[2]*School of Chemical and Bioprocess Engineering, University College Dublin, Belfield, Dublin 4, Ireland*
[*]*paul.jhimli@gmail.com (J.Paul Guin),* [*]*james.sullivan@ucd.ie (J.A. Sullivan)*

Keywords: Non-thermal-plasma, PFAS, Perfluorooctanoic acid, Hydroxyl radicals

Introduction

Fluoroalkyl compounds are used in a range of industries, household products and fire-fighting equipment. Due to their resistance to decomposition they are often known as forever chemicals [1]. Conventional water treatment plants fail to degrade them leading to eventual accumulation in the environment. The use of non-thermal plasma (NTP) is emerging as an effective Advanced Oxidation Process for their degradation in aqueous media.

Experimental

The NTP discharge apparatus consists of a copper cathode and stainless steel anode (Fig. 1). A vial containing 1 ppm aqueous PFOA with a dispersed alumina catalyst (Al_2O_3) was placed on a grounded anode. The cathode was placed perpendicular at a distance of 5 mm from the water surface. PFOA degradation was determined by negative ion ESI quadrupole time-of-flight MS (Agilent 6546 LC/Q-TOF).

Results and discussion

Figure 2 shows the degradation of PFOA (a model per-fluoro alkyl compoud) obtained after 20 min of plasma treatment in the absence (25%) and presence of catalyst (complete degradation). The degradtion products obtained in the process are also presented in figure 2. High energy electrons generated during plasma discharge interact with water and produce a mixture of reactive species (e^-, $HO^\bullet$, $H^\bullet$, $O_2^{\bullet-}$, H_2O_2 O_3, H_3O^+ H^+ O^+ O^-) and UV radiation [2,3].

The effect of the presence of a solid phase catalyst is clear and the higher degradation efficiency of PFOA in the presence of catalyst could be ascribed to several effects. Photocatalysis is unlikely given the bandgap of Al_2O_3 but electron impact upon the surface generating electron-hole pairs which may generate $^\bullet OH$ and $O_2^{\bullet-}$ radicals increases the level of PFOA degradation [2,4].

In addition, the catalyst may create plasma microdischarges inside its pores increasing the production of reactive species [2]. No change of the physico-chemical properties of the catalyst has been observed after plasma treatement (specifically using UV Vis and XPS analysis).

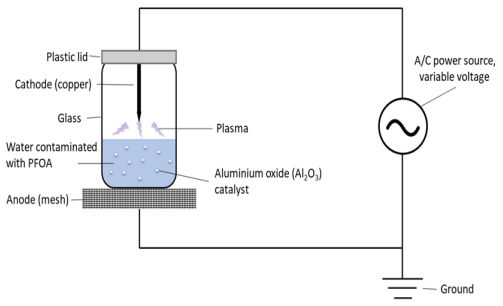

Fig. 1 Non-thermal plasma reactor set up

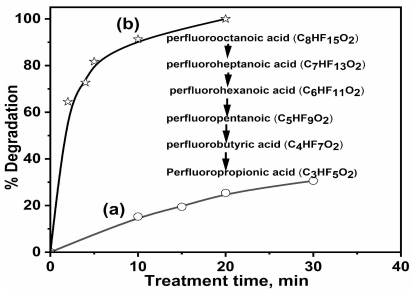

Fig. 2 (%) PFOA degradation in the absence (a) and presence (b) of Al_2O_3 after NTP treatment

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TiO_2 coating on PET nonwovens by dip-coating for photocatalytic effects

Park Jeong Jin[1], Lee Dong Kyu[1], Park Jin Won[1] and Lee Seung Goo[1*]

[1] *Department of Organic Materials Engineering, Chungnam National University, Daejeon, 34134, Republic of Korea*

[*] *lsgoo@cnu.ac.kr*

Keywords: PET nonwoven , TiO_2, Photocatalysis, dip coating

Introduction.

In recent years, as water pollution caused by industrial development has become serious, the importance of water filters has increased. Among them, titanium dioxide (TiO_2), a representative photocatalytic material, has shown excellent performance in removing pollutants due to its strong oxidation power through light irradiation [1]. It is applied to remove pollutants by coating on a support, especially in water treatment devices, but has the disadvantage of limited surface area. Powder type photocatalysts are also used, but they have the disadvantage of requiring a separation and collection process as well as economic disadvantage.

Polyethylene terephthalate (PET) nonwovens with network structure are used as filters due to their low cost and high mechanical strength [2]. In this study, needle-punched PET nonwovens were coated with TiO_2 to maximize their surface area, thereby maximizing their photocatalytic properties.

Experimental/methodology.

The coating of TiO_2 was carried out by dip coating method. The dip coating method uses taitanium (III) chloride ($TiCl_3$) as a precursor and has been reported to form TiO_2 at low temperatures [3]. Therefore, PET nonwovens were immersed in a $TiCl_3$ aqueous solution and reacted at a low temperature for 24 h to form TiO_2. The unreacted material was then washed and dried to obtain coated nonwovens.

Results and discussion.

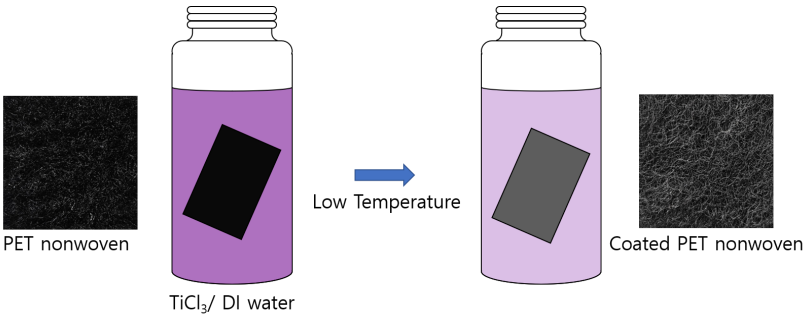

Figure. 1. Scheme of TiO_2 dip coating process on PET nonwoven

After coating, the nonwoven fabric was coated with white-colored TiO_2. The coated nonwoven fabric was then weighed to calculate the weight gain before and after. FT-IR analysis showed that the peak of TiO_2 appeared throughout, confirming that TiO_2 was coated. To confirm the photocatalytic properties of the coated PET, an organic matter degradation experiment was conducted. UV-VIS analysis was performed to confirm the degradation of organic matter.

In this study, TiO_2 coating of PET nonwoven fabric was performed by dip coating method. TiO_2 coating was confirmed. As a result, it can be expected to be applied to a simple and effective water treatment PET filter through photocatalytic reaction.

Acknowledgments

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Catalytic pyrolysis can offer a means to upcycle micro/nano plastics released from synthetic fibres during laundering

Silvia Parrilla-Lahoz[1], Marielis C. Zambrano[2], Vlad Stolojan[1], Rachida Bance-Soualhi[1], Joel J. Pawlak[2], Richard A. Venditti[2], Tomas Ramirez Reina[1,3], Melis S. Duyar[1]*

[1] *School of Chemistry and Chemical Engineering, University of Surrey, Guildford, GU2 7XH, UK.*

[2] *Department of Forest Biomaterials, College of Natural Resources, North Carolina State University, Raleigh, North Carolina 27695-8005, United States.*

[3] *Inorganic Chemistry Department & Material Science Institute, University of Seville-CSIC, Avda. Américo Vespucio 49, Sevilla, 41092, Spain.*

**m.duyar@surrey.ac.uk*

Keywords: Micro/nano plastics, Upcycling, recycling, thermochemical conversion, pyrolysis, gasification.

Introduction. Plastics are produced primarily from fossil fuels; the transition to a carbon-neutral economy will necessitate significant life cycle changes for plastics. Micro/nano plastics are generated when synthetic textile fibers are washed, endangering the environment. Pyrolysis is an emerging approach for waste valorisation, aimed at producing carbon materials and hydrogen [1]. Herein we demonstrate the use of a catalytic-packed bed reactor to co-produce solid carbon nanomaterials alongside hydrogen from both synthetic and natural textile derived micro/nano fibres.

Experimental/methodology. Bimetallic Ni-Fe catalyst with a molar ratio of 1:3 (10% metal loading) supported on γ-Al_2O_3 was prepared by a wet impregnation synthesis method. Catalytic-pyrolysis of cotton and PET was carried out in a one-stage, fixed bed reactor. Interlock fabrics without finishing were provided by Cotton Incorporated. Prior to the reaction, the fibres were reduced to microfibres. The quartz reactor was loaded with a pre-mix of 30 mg of textile microfibre and 15 mg of the catalyst. Pyrolysis was carried out in Ar (99.99% purity, 110 ml/min) at 500 °C, at a heating rate of 10 °C/min and held at 500 °C for 30 min.

Results and discussion. H_2 was produced when Ni-Fe catalysts were used to pyrolyze PET and Cotton textile microfibers, with the maximum production value attained at 500°C for both samples (Figure 1). The production of H_2 occurs at a higher temperature than the production of hydrocarbon products, which may be the result of catalyst reduction and subsequent hydrocarbon gas-phase cracking. The FT-IR spectrum demonstrates that thermal treatment altered the chemical functionalities and, consequently, the chemical composition of both samples. In addition, the TGA data show a distinct reduction of C-O-R chemical functionalities, which could be due to the decomposition of ethers, lactones, phenols, etc [1].

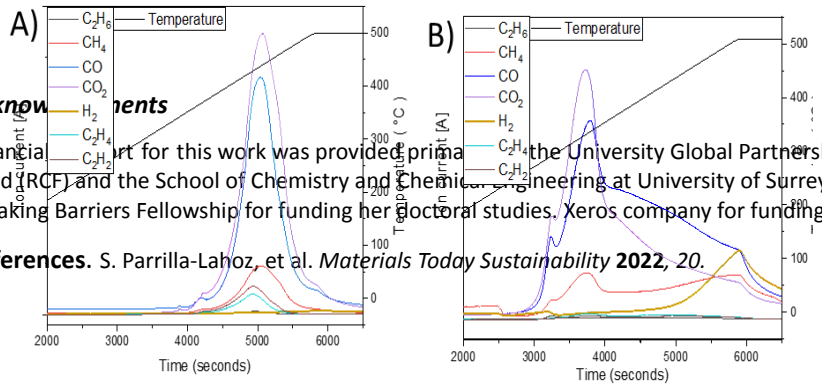

Figure 1. Gas releasing behaviors during catalytic pyrolysis process of A) Polyester microfibers and B) Cotton microfibers.

Acknowledgements

Financial support for this work was provided primarily by the University Global Partnership Network (UGPN) Research Collaboration Fund (RCF) and the School of Chemistry and Chemical Engineering at University of Surrey. SPL acknowledges the University of Surrey Breaking Barriers Fellowship for funding her doctoral studies. Xeros company for funding part of the project.

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Catalytic hydrogenation of water pollutants by platinum metal catalysts

A. Plá-Hernández[1*], A.E. Palomares Gimeno[1], F. Rey[1]

[1]*Instituto de Tecnología Química, Universidad Politécnica de Valencia - Consejo Superior Investigaciones Científicas, Avenida de los Naranjos s/n, 46022, Valencia, España)*
[*]Corresponding author: *adplher@itq.upv.es*

Introduction. Water is a fundamental resource and is necessary to guarantee its quality, mainly when it is used for human consumption [1]. Most disinfection treatments are based on the use of chlorine compounds such as chlorine dioxide. However, this process can produce by-products such as chlorite, chlorate and bromate [2] that have negative effects on health. For these reasons, the World Health Organization set a limit for these pollutants in drinking water. An interesting alternative for the removal of these water pollutants from water is the catalytic reduction with hydrogen. In this reaction ClO_3^- and BrO_3^- are reduced to innocuous products such as Cl^- and Br^-.

Experimental/methodology. Catalysts were prepared by incorporating platinum to different metal oxides using different processes. After the addition of the Pt-precursor, the material was calcined at 350ºC and activated with hydrogen at 200ºC. The experiments were performed in a batch stirred tank reactor at room temperature and atmospheric pressure, using hydrogen as reducing agent. The typical experiments were made with 1 g of catalyst and 0,6 L of polluted water with 50 ppm of chlorate/bromate. The analysis of the reactants and products was made by ionic chromatography. The catalysts were characterized with different techniques such as inductively coupled plasma (ICP), X-ray diffraction (XRD), hydrogen chemisorption, temperature programmed reduction (TPR), N_2 adsorption and scanning electron microscopy (SEM).

Results and discussion. The catalytic study was carried out using platinum supported on different materials and prepared by different procedures. The results obtained with the catalysts supported on Al_2O_3 showed an important influence of the metal precursor calcination temperature on the catalytic activity, obtaining the best results with the catalysts calcined at 350ºC, decreasing the activity when the catalyst was calcined at higher temperatures. These results have been related with a higher platinum dispersion at lower calcination temperature, as it was observed by characterizing the catalysts with H_2 chemisorption and electron microscopy. The influence of the support on the catalytic activity was studied with platinum catalysts supported on Al_2O_3, TiO_2 and zeolites. The use of zeolites as catalytic support showed that the topology, the Si/Al ratio and the amount of sodium are the main factors influencing the catalytic activity. The best results are obtained with the Pt catalysts supported on zeolites that contain a higher number of acid centres, with accessible structures and with low sodium content. These characteristics improve the dispersion of platinum and enhance the interaction of the reactants with the active sites. In this way, the best results were obtained with the catalyst supported on FAU with a Si/Al ratio of 6. On the other hand, the use of TiO_2 as a support was also studied in presence and in absence of light. In presence of light, an improved catalytic activity was observed, decreasing it in darkness. These results indicate the presence of a photocatalytic reduction of chlorates that increases the catalyst activity, obtaining in these conditions and with this support the best activity. Finally, the influence of the reaction media temperature on the catalyst activity was studied obtaining better results when decreasing the water temperature, due to the higher solubility of hydrogen in water. These results show that it is possible to remove water pollutants such as chlorate by catalytic reduction using Pt catalysts, but is necessary to tune the characteristics of the support that enhance the platinum dispersion and improve the catalytic processes.

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Microwave-hydrothermal assisted synthesis of $ZnFe_2O_4$/RGO nanocomposites for the removal of organic pollutants from wastewater

Kun-Yauh Shih[1*], En-Rui Wang[1]

[1]*Department of Applied Chemistry, National Pingtung University, Pintung, Taiwan*
[*]*sky@mail.nptu.edu.tw*

Keywords: nanosorbent, $ZnFe_2O_4$/RGO, nanocomposites

Introduction. Nearly 200 years of industrial development have led to environmental pollution. Dyes from pharmaceutical and other industries are major organic pollutants. Organic dyes are not easily decomposed in the natural environment due to their stable and complex chemical structure. Dye molecules may block sunlight from entering the water and reduce the level of dissolved oxygen in the water system. Therefore, the removal of organic dye molecules from industrial and municipal wastewater has become a very important issue. The high specific surface area and the special chemical structure of $ZnFe_2O_4$/RGO nanomaterials allow them to optimize water quality by adsorbing large amounts of organic pollutants in water through electrostatic attraction and π-π interaction with the aromatic region of dye molecules. The main purpose of this study was to prepare $ZnFe_2O_4$/RGO magnetic nanoparticles by microwave hydrothermal method using a combination of low-toxicity zinc ferrite and reduced graphene oxide. The dye adsorption mechanism of this nanosorbent was investigated by using $ZnFe_2O_4$/RGO to adsorb hazardous MB dyes.

Experimental/methodology. GO was prepared using H_2SO_4 and $KMnO_4$ as oxidizing agents and synthesized from natural graphite powder by a modified Hummers method. To synthesize the ZFG nanosorbent, 50 mg GO was dispersed in 30 mL of deionized water at room temperature. After adding 0.42 mmol $Fe(NO_3)_3$ and 0.21 mmol $Zn(NO_3)_2$, the solution was sonicated for 30 min and the pH of the solution was adjusted to 12 with 2 M NaOH. After sonication for 15 min, the solution was transferred to a Teflon-lined container and the samples were heated using the microwave. The heating temperature was controlled at 140, 160, 180, and 200 °C to synthesize the various materials of $ZnFe_2O_4$/RGO. Finally, the $ZnFe_2O_4$/RGO is filtered and dried in an oven at 75 °C for 12 hours.

Results and discussion. Raman spectra show that spinel-type ZF and ZFG exhibit similar features in the low-frequency region (100-1000 cm -1) corresponding to the A_{1g} symmetric and F_{2g} asymmetric modes of spinel-type $ZnFe_2O_4$. GO, RGO and $ZnFe_2O_4$/RGO have two obvious peaks near 1341 and 1589 cm^{-1} that belong to the D-band and G-band of the Raman spectrum of graphene, respectively. The intensity ratio of D band to G band (I_D /I_G) of RGO and all $ZnFe_2O_4$/RGO is higher than the GO. This means that RGO and $ZnFe_2O_4$/RGO have more surface defects. For the RGO and $ZnFe_2O_4$/RGO FT-IR spectra, the absorption band at 1550 cm -1 is the C=C skeleton stretching vibration of the graphene structure. The absorption bands at 850 to 956cm-1 are overlapping regions of epoxide, hydroxyl, C=O contribution, and carboxyl group. TEM showed that $ZnFe_2O_4$ nanoparticles had the smallest particle size and narrow distribution width at 180℃, which is consistent with the results that shorter nucleation and crystallization times can produce small particle size and high dispersion.

The adsorption capacity and dye removal efficiency of $ZnFe_2O_4$, RGO, and various $ZnFe_2O_4$/RGO nanomaterials on MB solutions was investigated. The results showed that the adsorption capacity and removal efficiency of dyes increased rapidly with time in the first 3 min. and decreased significantly after 3 min. In addition, the theoretical maximum adsorption capacity of ZFG-18 calculated using the Langmuir model was 212.77 mg g^{-1} higher than that of $ZnFe_2O_4$, RGO, and other $ZnFe_2O_4$/RGO. Two main mechanisms of the MB adsorption process were observed by FT-IR, Raman spectroscopy, and adsorption measurements at different pH values. The first mechanism is the electrostatic interaction between the MB dye = N + H group and the residual oxygen functional groups of RGO. The second mechanism is the π-π interaction between the RGO carbon skeleton and the dye molecules. VSM measurement and recovery tests show that $ZnFe_2O_4$/RGO can be separated with magnets and has a long recovery life. Therefore, $ZnFe_2O_4$/RGO has potential application in wastewater treatment.

Catalytic pyrolysis of single-use plastic waste over hierarchical zeolite to obtain fuel grade hydrocarbons

Subhashini[1], Tarak Mondal[1,*]

[1,*] Department of Chemical Engineering, Indian Institute of Technology, Ropar, India.

[*]*E-mail: tarakmondal@iitrpr.ac.in*

Keywords: Single-use plastic, herarchical ZSM-5, catalytic pyrolysis, fixed-bed reactor

Introduction. Municipal solid waste management has been one of the most pivotal factors that affect the environmental health terribly. Plastic waste contributes around 13% of total municipal solid waste. Plastic waste management has gained global awareness and thus recycling such massive quantities is targeted. Catalytic pyrolysis has been the most suitable approach to convert the waste plastic into a source of energy and chemicals. The use of catalyst also helps to lower the energy requirement of the process as well as the residence time. Zeolite catalysts are used for their key features i.e., thermal stability, acid strength, pore size and pore distribution. Zeolites with mesopores and micropores are also favourable because primary cracking of polymer molecules of plastics occurs in mesoporous surfaces and then further cracking over microporous surfaces leads to small chain hydrocarbons.

Experimental/methodology. The hierarchical zeolite catalyst was synthesized by hydrothermal method to carry out the catalytic pyrolysis reaction of the waste plastic polymers and obtain smaller fractions of the hydrocarbons in the range of fuel grade hydrocarbons. The catalytic pyrolysis reaction of the waste plastic polymers was carried out in a fixed bed reactor made of stainless steel under inert environment in an ex-situ manner with catalyst to waste ratio as 1:10.

Results and discussion. With the use of synthesized hierarchical zeolite the pyrolysis temperature for various waste plastic reduced to the range of 400-450℃ as compared with the thermal degradation, and produced desired fuel range liquid oil. The synthesized hierarchical zeolite catalyst has also shown comparable selectivity towards the production of C9 - C20 range hydrocarbons. The obtained liquid oil components were determined by using GC-MS and the major components were alkanes, alkenes, aromatics, ketones and a few aldehydes. Presence of these functional groups was confirmed by the FTIR and proton NMR analysis of the liquid oil.

Acknowledgments

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The influence of ferrocene anchoring method on the reactivity and stability of SBA-15-based catalysts in degradation of ciprofloxacin via photo-Fenton process

A. Walkowiak*, L. Wolski, M. Ziolek

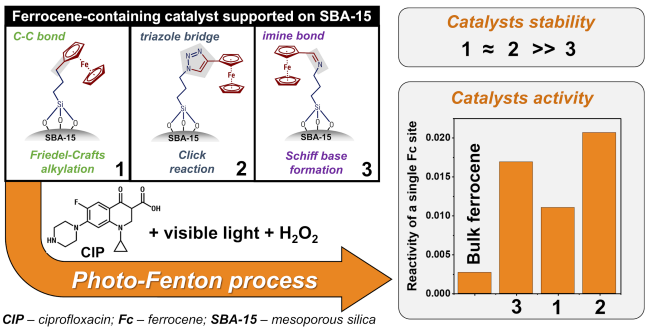
Adam Mickiewicz University, Poznań, Faculty of Chemistry,
Department of Heterogeneous Catalysis, ul. Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland
**adrian.walkowiak@amu.edu.pl*

Keywords: Advanced oxidation processes; photo-assisted degradation of antibiotics; H_2O_2; ferrocene.

Introduction. Ferrocene (Fc) is a stable organometallic iron compound which can activate H_2O_2 toward the formation of reactive oxygen species (ROS; e.g. hydroxyl radicals) through the so-called Fenton reaction [1]. An important feature of Fc is its strong light absorption in the UV-Vis range. It makes this compound an attractive candidate for visible-light-driven photo-Fenton processes which have been frequently reported as much more efficient than typical Fenton reactions [2]. Photo-Fenton reaction is an example of Advanced Oxidation Processes which are a group of methods highly efficient in the removal of organic pollutants, such as antibiotics, whose steadily growing production and consumption entails severe environmental and medical issues [1]. In this study, different ferrocene-containing materials were prepared via post-synthetic modification of mesoporous SBA-15 silica. As-prepared composites were addressed to the catalytic degradation of ciprofloxacin (CIP), a model antibiotic pollutant, in the presence of H_2O_2 and/or visible light.

Experimental/methodology. First, SBA-15 silica was functionalized using selected organosilanes and then Fc (or its derivative) was anchored using three various procedures, namely: i) Schiff base formation, ii) Friedel-Crafts alkylation, and iii) click reaction (azide-alkyne cycloaddition) (see Fig. 1). The prepared materials were thoroughly characterized with the use of XRD, N_2 physisorption, FTIR, DR-UV-Vis and XPS. The reactivity and stability of the as-prepared hybrid organic-inorganic materials in CIP degradation via photocatalytic, Fenton and photo-assisted Fenton processes were examined, and the degradation efficiency was evaluated spectrophotometrically.

Results and discussion. Results obtained in this study showed that Fc anchoring method had a significant impact on the efficiency of Fc anchoring as well as the reactivity and stability of SBA-15-based catalysts. As concerns the reactivity of a single Fc active site in the photo-Fenton process, the most reactive were Fc species from the catalyst prepared by click reaction (formation of triazole ring). Moreover, it was found that the catalysts prepared by the click reaction and Friedel-Crafts alkylation were much more stable in three subsequent reaction cycles than the catalysts prepared via Schiff base formation. Based on the above, it was established that the most promising method for the preparation of SBA-15-based catalysts for the degradation of CIP via the photo-Fenton process is the click reaction. Fc species anchored via this method on the siliceous support are not only the most reactive but also exhibit the highest long-term stability under the working conditions applied in this work. More details will be delivered during the presentation.



Acknowledgments

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Valorization of waste materials resulting from the chemical conversion of biomass using tailormade polyoxometalate catalysts

André Wassenberg[1]*, Tobias Esser[1], Maximilian J. Poller[1] and Jakob Albert[1]
[1]*1Institute for Technical and Macromolecular Chemistry, University of Hamburg, 20146 Hamburg, Germany*
*andre.wassenberg@uni-hamburg.de

Keywords: sustainable chemistry, green catalysis, waste valorization, humins, polyoxometalates, biomass, synthesis and characterization

Introduction

Sustainability is one of the most important aspects of modern chemical research, as our dependence on finite fossil raw materials is not feasible in the long term. Therefore, alternative and easily available raw materials must be found to replace fossil raw materials as fuels or bulk chemicals. A sustainable and cheap option for this is biomass. However, the conversion of biomass into platform chemicals, such as the conversion of cellulose to levulinic acid, often produces unwanted by-products, like humins. Humins are black, polymeric solids that are insoluble in common solvents.[1] They are often formed from sugar based biomass under acidic conditions and high temperatures. These solids pose a problem, as their formation is unavoidable, they are a waste of raw materials, and by clogging reactors and catalysts they cause damage to chemical plants and safety issues. [2]

In our research, we have investigated the valorization of humins by catalytic conversion into low molecular weight carboxylic acids like formic acid (Figure 1). This will make the conversion of biomass into platform chemicals more efficient and prevents formation of undesired by-products.

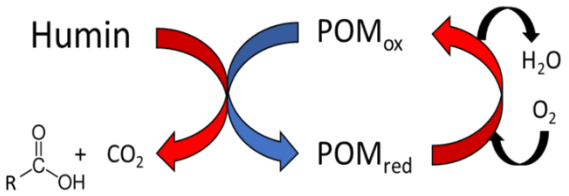

Figure 1: Simplified catalytic cycle for the conversion of humins using polyoxometalate (POM) catalysts.

Experimental

All reactions were carried out in a 10-fold oxidation system with ten 20 mL hastelloy reactors capable of pressures up to 80 bar and temperatures up to 200 °C. A variety of different humins were prepared from different sugars to simultaneously study the effect of different reaction conditions on humin formation and subsequent conversion. Polyoxometalates, which were synthesized in our research group, were used as catalysts for the oxidative conversion of the humins. Liquid phase analysis was carried out using NMR spectroscopy and GC-MS.Moreover, gas phase analysis was done via offline GC.

Results and discussion

In our experiments we have sucessfully converted up to 50 % of the humic mass. The main products were formic acid, acetic acid and carbon dioxide. The highest conversions were shown by humins that were synthesized in acetic acid, which is an ideal solvent for most of the industrial processes that produce humins as a by-product.

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Ion Exchange and Dealumination of Large Faujasite Crystals

Y. Ganjkhanlou[1], S. Rejman[1], J. Heesakkers[1], J. V. Emst[1], W.C. Versluis[1], J.M. Dorresteijn[1], I. Vollmer[1], E.T.C. Vogt[1], B.M. Weckhuysen[1], F. Meirer[1*]

[1]*Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science and Institute for Sustainable and Circular Chemistry, Utrecht University, 3584 CG Utrecht, The Netherlands*

[*]*F.Meirer@uu.nl*

Keywords: Faujasite, Zeolite, Diffusion, Cracking, Plastics

Introduction. Zeolite Y is a commonly utilized molecular sieve in various catalytic processes, such as fluid catalytic cracking (FCC) [1], hydrocracking, biomass upgrading [2], and, more recently, the depolymerization of plastics into aromatics [3]. Understanding ion exchange, diffusion, and dealumination processes is critical for gaining insights into activity and stability of zeolite Y during different catalytic reactions. While fluorescent probes have been developed to examine intracrystalline diffusion in other zeolites, such as ZSM-5 and β [4], this has not yet been done for zeolite Y. For such studies, large zeolite crystals are required, but the preparation of large crystals of zeolite Y using traditional methods can be costly [5] and, in some cases, involve the use of non-benign structure directing agents (SDAs) [6].

Experimental/methodology. In this study, we first synthesized large zeolite Y crystals with sizes of ~ 50 µm using simple and readily available precursors and replaced the reported SDAs with a more environmentally friendly and more economical one (i.e., choline chloride) as it is used in e.g., animal feed. We performed ion exchange using ammonium nitrate (AN) and ammonium oxalate (AO). After calcination, the AN treated sample was dealuminated by steaming and acid leaching. We then studied not only the morphology and structure of the crystals, but also intracrystalline diffusion inside the bipyramidal zeolite crystals using various fluorescent probes. Finally, we followed the cracking of plastic (i.e., polypropylene, M_W = 6,000 g/mol) over the crystals using in-situ confocal fluorescence microscopy (CFM).

Results and discussion. Using different characterization techniques, we can conclude that dealumination by steaming/acid leaching is structure related (as evidenced by triangular features in both SEM and CFM images of the coked crystals-Fig. 1a-c), while dealumination which occurred simultaneously during the ammonium exchange by AO is defect-related and forms macro-meso pores inside the crystals (Fig. 1d-f).

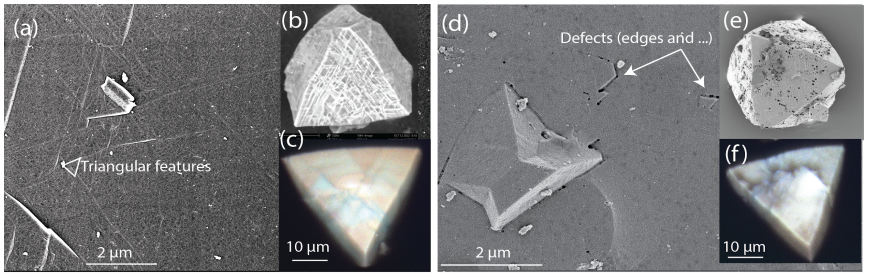

Fig. 1 (a, b) SEM and (c) CFM images of steamed HY zeolite crystals-presence of structure related features, (d, e) SEM and (f) CFM images of AO treated crystals-presence of isotropic pores near defect. CFM images of fluorescence coke species are obtained using 405 nm laser excitation on coked crystals after plastic cracking at 250 °C for 20 min.

Acknowledgments

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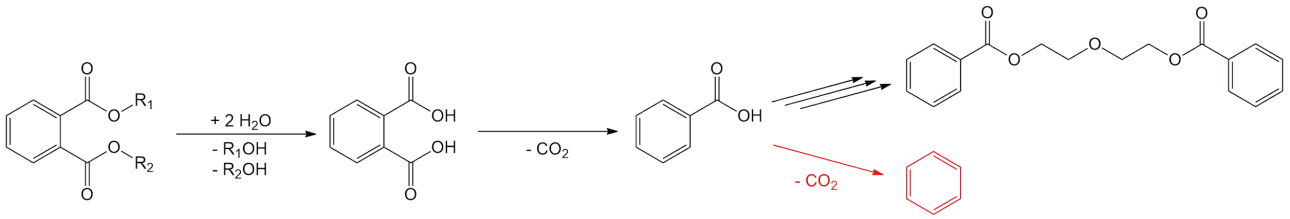
The detoxification and revalorisation of plastic-waste extracted phthalate plasticizers into safe alternatives

Simon Windels[1], Wouter Stuyck[1] and Dirk E. De Vos[1]

[1]*Centre for Membrane Separations, Adsorption, Catalysis and Spectroscopy, KU Leuven, Leuven, Belgium*
[*]*dirk.devos@kuleuven.be*

Keywords: Waste valorization, Legacy additives, Plasticizers, Detoxification

Introduction. In light of emerging PVC recycling techniques, large amounts of endocrine disruptive phthalates are expected to become available in the near future as hazardous waste streams. These legacy additives have been dominating the global plasticizer market, however they are gradually being replaced by safer alternatives. [1] In light of this transition, we recently developed a process in which real post-consumer waste-extracted phthalate plasticizers were hydrogenated into safe cyclohexanedicarboxylate plasticizers, such as DINCH. [2] However, based on the intrinsic value of aromatics, the loss of this functionality can be considered adverse, leading us to prioritize its preservation in this work. More specifically, benzoic acid was selectively obtained from the one-pot hydrolysis-decarboxylation of
end-of-life phthalate plasticizers, carefully avoiding the overdecarboxylation to benzene. In support of a



circular plastic economy, this drop-in chemical could be simply purified and employed in the production of industrially relevant benzoate plasticizers, such as diethylene glycol dibenzoate.

Experimental/methodology. All reactions were performed in a 50 mL high-pressure Parr® reactor vessel at elevated temperature (100 °C – 250 °C) under an inert atmosphere (N_2). The experiments were stopped by fast cooling of the reactor in an ice-in-water bath. The reaction samples were analyzed by
High-performance liquid chromatography (HPLC) and Proton nuclear magnetic resonance (^{1}H-NMR).

Results and discussion. The decarboxylation of phthalic acid in water was investigated in an initial series of experiments, which revealed that noble metals catalyze both the decarboxylation to benzoic acid as the subsequent conversion to benzene under similar reaction conditions. Despite vastly different adsorption characteristics for aromatics, the maximum obtained yield of benzoic acid seemed to be independent of the noble metal. In contrast,
Cu-catalyzed decarboxylations showed a completely deviating reaction profile as the conversion rate of phthalic acid was not only remarkably higher but the consecutive decarboxylation did not proceed, yielding

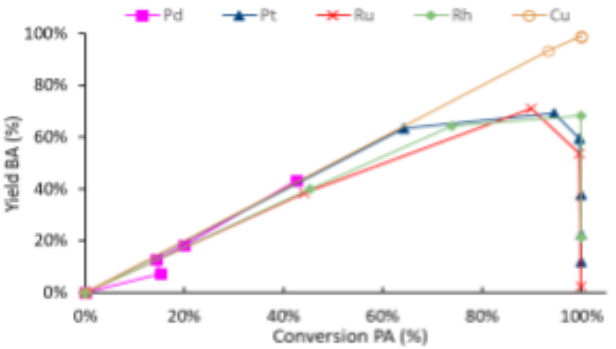


Fig: Metal-catalyzed decarboxylation of phthalic acid

> 99% benzoic acid. In light of the green chemistry principles, telescoping of this decarboxylation reaction with a preceding hydrolysis of (plastic waste-extracted) phthalate plasticizers was pursued. To that end, the effect of the hydrolysis catalyst (acid or base), residual PVC (and impurities) and the alcohol side-chains on the decarboxylation was evaluated. To illustrate our proposed revaluation strategy, an industrially relevant benzoate plasticizer was synthesized in high yields from such waste-extracted phthalate esters, in which no excessive purification of the intermediates was required.

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Experiment and theory of catalytic reactions

Tools for Navigating Catalyst Landscapes

Shubhajit Das*, Ruben Laplaza, J. Terence Blaskovits, Clémence Corminboeuf

Laboratory for Computational Molecular Design, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland
** shubhajit.das@epfl.ch*

Keywords: scaling relationships, volcano plots, inverse design, CO_2 reduction, pincer complexes, frustrated Lewis pairs

Introduction.

Developing and implementing tools for rapid estimation of catalyst performance can significantly expand the search space and accelerate the discovery process. To this end, we present a computational framework aimed at accelerating the exploration/optimization of catalyst landscapes by combining concepts from physical-organic chemistry, statistical techniques, and genetic optimization algorithms.

Methodology.

Our approach typically relies on establishing linear and nonlinear scaling relationships for mapping the chemistry/geometry of the active site of catalysts to their performance through intuitive electronic/structural descriptor variables. The resulting volcano plots/activity maps[1] then guide us to recognize "sweet spots" in the respective descriptor spaces that fulfill the criteria for maximum activity/selectivity. Leveraging this information, we perform straightforward “direct” screening of large libraries of catalysts to identify the ones with desired properties. Additionally, the maps are also utilized in a genetic algorithm-based catalyst optimization pipeline enabling the “inverse” design of candidates.

Results and discussion.

We demonstrate the efficacy of the toolkit in identifying catalysts with improved activity/selectivity for industrially important chemical processes involving CO_2 reduction. We focus on two case studies.

In the first one, we aim to predict the selectivity of first-row transition metal pincer catalysts for stepwise hydrosilylation of CO_2 to formic acid, formaldehyde, or methanol level.[2] Here, the hydride affinity of the catalysts is used as a descriptor to capture the selectivity trends in a composite volcano picture allowing the identification of metal/ligand combinations for accessing a particular product level. These predicted trends were validated experimentally.

The second case study focuses on the challenging discovery of frustrated Lewis pairs (FLPs) for the direct catalytic hydrogenation of CO_2.[3,4] Here, we map the chemical and geometrical compositions of FLPs to their activity using the Lewis strength of the components and their relative spatial arrangements. The predicted FLP combinations from the maps are experimentally validated to achieve the first reports of catalytic turnovers in this reaction.[3] Utilizing the chemistry and the geometry-based tools together, we not only perform a direct screening of curated databases of FLPs but also implement a genetic optimization pipeline for identifying promising candidates with desired catalytic properties. Finally, analysis of these leading candidates enables the formulation of pragmatic and experimentally relevant design principles for further exploration of FLP-based catalysis.

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Computing catalytic reaction times and paths with machine learning and rare events sampling methods

T. Pigeon [*1,2], G. Stoltz[1], M. Corral-Valero[2], A. Anciaux-Sedrakian[3], T. Lelièvre[1], P. Raybaud[2]

[1] *CERMICS, Ecole des Ponts ParisTech, 6/8 av. Blaise Pascal - Cité Descartes, 77455 Marne-La-Vallée, FRANCE and Equipe-projet MATHERIALS, Inria Paris, 2 rue Simone Iff, CS 42112 75589 Paris Cedex 12*

[2] *IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP3, 69360 Solaize, France*

[3] *IFP Energies nouvelles, 1-4 Avenue du Bois Préau, 92852 Rueil-Malmaison, France*

[*] *Email: thomas.pigeon@inria.fr*

Keywords: Machine Learning, reaction rate, rare events, reactive trajectories

Introduction. Determining reaction paths and rates are one of the key points required to accurately characterize catalytic reactions. As there are generally many elementary steps and intermediates during such transformations, it is difficult to determine reliable reaction constants from theoretical simulations based on harmonic transition state theory. Methods have been devised to overcome this limitation. In our work, we explore a rare events simulation method called Adaptive Multilevel Splitting (AMS)[1], combined with ab initio molecular dynamics to sample reactive trajectories. Thanks to the Hill relation[2], we propose a way to theoretically compute unbiased reaction times and paths.

Experimental/methodology. The Hill relation requires to estimate the probability of reaching the product state before coming back to the reactant. To estimate the probability of such a rare event, it is split in the succession of multiple more likely sub-event (see Figure 1.a inset). The AMS algorithm was implemented in combination with a periodic plane-wave DFT (VASP) software. The progress of the transition is quantified using a one-dimensional Reaction Coordinate (RC) to place the splitting levels (see Figure 1.a). The RC along with the definitions of reactant and product states are built using supervised machine learning tools and unbiased molecular dynamics.

Results and discussion. The proposed method is applied on the case study of the conformations and dissociations of water on the (100) γ-alumina surface. Reaction rate constants are compared to those obtained via harmonic transition state theory (hTST). The reactive trajectories are classified using clustering methods allowing to differentiate reaction mechanisms. The sampled reactive trajectories are analyzed to identify TS structures in the sense of equal probability of reaching the product and reactant state, see Figure 1 b). Although the TS structures of water dissociation are rather similar, we find that the rate constant calculated with AMS can be two orders of magnitude smaller than the value obtained with hTST (Figure 1 c). This discrepancy is attributed to entropic effects which are better taken into account with AMS.

We believe that this method provides an innovative way for better quantifying reaction rates, and extensions to more complex reaction mechanisms are currently investigated.

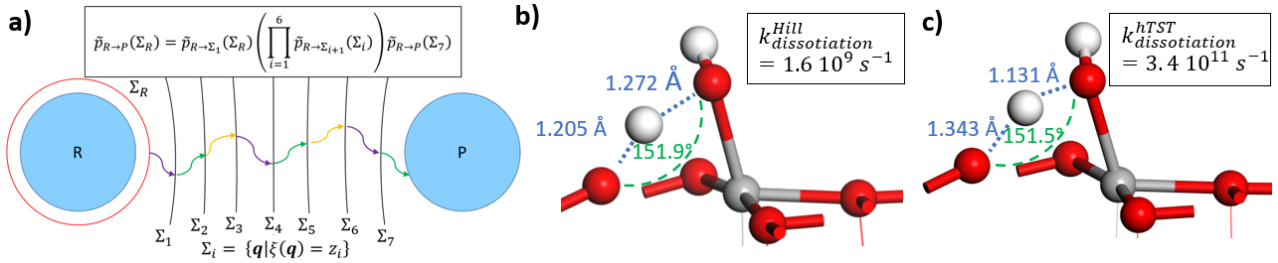

Figure 1: a) Illustration of multiple levels of a reaction coordinate placed between the reactant state and product splitting the rare event into multiple more likely ones. The inset displays the expression of the probability estimator. **b)** Average transition structure sampled with AMS. The inset corresponds to the estimated rate constant calculated with the Hill relation. **c)** Saddle point on the potential energy surface according to hTST. The inset corresponds to the estimated rate constant calculated with hTST.

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Principles of Spin Catalysis

J. Gracia[1*], M. Fianchini[1], C. Biz[1]

[1]*Magnetocat SL, Alicante, Spain*
[*]*jose.gracia@magnetocat.com*

Keywords: spin catalysis, magnetic catalysts, strongly correlated materials, quantum spin exchange

Introduction. Strongly correlated electrons enhance the activity of certain catalysts. Understanding "why" and "how" is strictly dependent on understanding complex quantum phenomena, like metal− insulator transitions and ferromagnetism. An improved fundamental view of the quantum interactions (correlations) lets us uncover additional details of the most relevant spin electronic factors in catalysis and their origin, nature, and influence. The importance of this fundamental research on orbital magnetism and spin-potentials is not only confined to a pure academic scientific domain but, being deeply intertwined, as it is, with the efficiency of electrocatalytic processes and technologies for the production of green hydrogen, it bears a tremendous impact on the idea of a cleaner and more sustainable world.

Experimental/methodology. Theoretical work about the new advances about the role of spin-potentials in electrocatalysis.

Results and discussion. Quantum correlations have drastic effects on the energy of magnetic materials and thus in catalysis.[1] Just as spintronics deals with advanced spin-based technology and devices where both the charge and spin of the electrons are modulated to offer a wide diversity of functionalities, similarly, the idea that the surface reactivity may be modulated by the influence of cooperative spin potentials, in open shells via the orbital engineering of earth-abundant magnetic systems is a tangible reality. Strongly correlated electrons, in fact, can affect the efficiency, cost, implementation, and environmental footprint of any heterogeneous catalyst. Quantum spin exchange interactions (QSEI) are a subtle phenomenon lying outside of the domain of classical physics, however they are responsible for the unusual intrinsic properties of magnetic catalysts. The influence of cooperative QSEI in materials with unpaired electrons can be seen in their characteristic structure, electronic conductivity, chemical bonding,[2] catalytic activity, and selectivity.[3]

We mainly present the physics that describe and rationalize the quantomechanic origin of QSEI in open shells, showing how spin-potentials enhance the reaction mechanisms of magnetic catalysts. This improved theoretical description is the only path to understand all kind of catalysts, from weakly to strongly correlated. A complete treatment of orbital physics, synergistically integrated into classical catalytic concepts like the Sabatier's principle, promises to improve predictions in the design of future catalysts and technologies.

Acknowledgments
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Operando spatial reactor analysis and kinetic study of oxidative coupling of methane

J.Palomo, N. Koenraadt, J. de Kort, A. Urakawa*

Catalysis Engineering, Department of Chemical Engineering, Delft University of Technology, Delft, 2629 HZ, The Netherlands

* A.Urakawa@tudelft.nl

Keywords: OCM, *operando* thermal analysis, spatial reactor analysis, kinetic modeling.

Introduction. Oxidative Coupling of Methane (OCM) is a direct and exothermic reaction for the conversion of methane into ethane and ethylene. However, due to the high temperatures required for methane activation, deep oxidation reactions take also place, which lower the yield towards the desired C_{2+} products. In the last decades, a huge effort was put into the development of efficient catalysts. On the other hand, the number of studies dealing with understanding OCM reaction mechanism and kinetics is limited. OCM proceeds through a complex homogeneous-heterogeneous reaction network. In addition, the presence of both endothermic and exothermic reaction steps in OCM results in the apparition of temperature gradients in the catalyst bed [1]. This intrinsic complexity makes the elucidation of comprehensive kinetic models a challenge. In the present work, we examine the OCM reaction mechanism and kinetics, using *operando* spatial resolved reactor analysis techniques.

Experimental/methodology. MgO and La_2O_3 were used as catalysts. Spatially resolved temperature and concentration profiles under *operando* conditions, were obtained using a customized reactor system that allows gas sampling and temperature measurements at different axial reactor positions (1 µm precision). A thermal infrared camera was used to determine presence of localized thermal phenomena in catalyst bed. A comprehensive kinetic model was developed for the OCM process.

Results and discussion. IR thermography images of the catalyst bed showed temperature deviations as high as 100°C (see Figure 1a), evidencing the importance of these physical phenomena in the OCM process. Isothermal operation was achieved, in case of MgO catalyst, by physically mixing the catalyst with SiC. For kinetic study, 39 gas phase reactions and 8 heterogeneous surface reactions were considered. Kinetic and thermodynamic parameters for the heterogeneous elementary steps were estimated.

The kinetic model reproduced the experimental data with a high accuracy (Figure 1b). A rate analysis was carried out, being it feasible to estimate the importance of both the heterogeneous and homogeneous reactions in the overall OCM process.

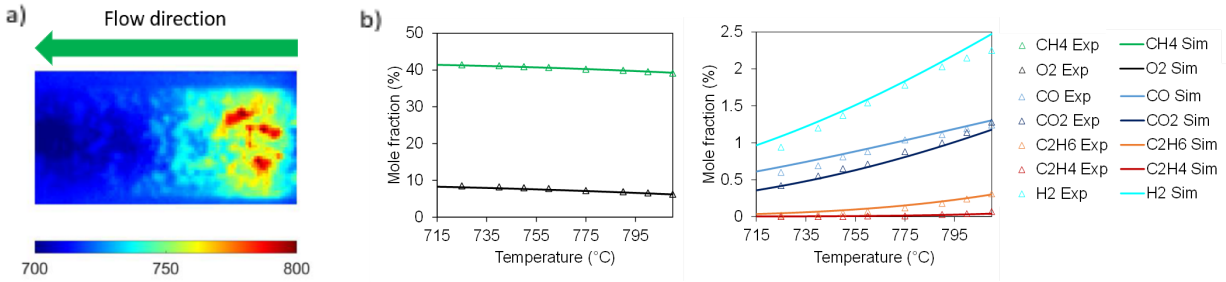

Figure 1. a) IR thermography of MgO catalyst bed, 700 °C, W_{cat} = 80 mg, W_{SiC} = 57 mg, $CH_4/O_{2,0}$= 4 and P_{CH4} = 40%, Fv = 150 mL min^{-1}. b) Reactant and products mole fractions as a function of temperature, W_{cat}= 15 mg, M_{SiC}= 250 mg, Fv = 150 mL min^{-1}, CH_4:O_2 = 4, P_{CH4} = 40%.

Acknowledgments

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Local structural changes of Mo_3VO_x by the heat treatment and its effects on propan ammoxidation

K. Shimoda[1*], S. Ishikawa[2], K. Shimizu[1], W. Ueda[2]

[1]*Institute for Catalysis, Hokkaido University, N-21, W-10 Kita-ku, Sapporo 001-0021, Japan*
[2]*Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan*
[*]*uedaw@kanagawa-u.ac.jp*

Keywords: crystalline Mo_3VO_x, propane ammoxidation, local structure

Introduction. Crystalline Mo-V-Te(Sb)-Nb oxide catalyst (MoVTe(Sb)NbO) has attracted much attention due to its outstanding catalytic performance for the ammoxidation of propane to form acrylonitrile (AN). This catalyst is constructed by the structural arrangement based on $\{Mo_5(Nb)O_{21}\}^{7-}$ pentagonal units and $\{MO_6\}$ (M = Mo,V) octahedral, forming hexagonal and heptagonal channel micropores in the crystal structure. Among these channels, Te or Sb is located mainly at the hexagonal channel and partly at the heptagonal channel. It is widely believed that its excellent catalytic properties are originated from the sophisticated structural arrangement in which the constituent elements are located in each specific structural site, allowing the cooperation of each catalytic function to realize the multi-step reactions. In fact, orthorhombic Mo_3VO_x catalyst (MoVO) having an identical crystal structure with MoVTe(Sb)NbO showed poor selectivity toward AN. In this study, we found that MoVO showed outstanding catalytic properties for the ammoxidation of propane without introducing Te, Sb, and Nb simply by heat-treating MoVO above 550 °C under inert gas flow.

Experimental/methodology. MoVO was synthesized by the repoted procedure.[1] MoVO-x was prepared by the heat treatment of MoVO at x °C under flowing 50 mL min^{-1} of N_2 (x: heat treatment temperature). Reaction conditions of propane ammoxidation: reaction temperature, 440 °C; catalyst amount, 0.05-0.6 g; reaction gas, $C_3H_8/O_2/NH_3/He$ = 1.2/2.9/1.5/14.4 mL min^{-1}.

Results and discussion. Effects of heat treatment temperatures on the propane ammoxidation were investigated using MoVO-x. Figure 1 shows the AN selectivity of various catalysts at the propane conversion of 47%−50%. When the heat treatment temperature was 450-500 °C, the selectivity to AN was 24.6%−31.3%, and was substantially lower than that of MoVTeNbO used as a comparison (AN selectivity, 62.6%). However, the AN selectivity increased drastically by simply increasing the heat-treatment temperature, and MoVO-600 showed a similar AN selectivity with MoVTeNbO at the similar propane conversion (AN selectivity, 56.7%). XRD measurements revealed that the crystal structure of MoVO changed only a little by the heat treatment below 500 °C. However, $V_{0.95}Mo_{0.97}O_5$ (VMo) phase started to segregate from MoVO above 550 °C. Since the contents of V in the VMo phase (V/Mo = 0.98) is larger than that of MoVO (V/Mo = 0.37), it was found that V is preferentially removed from the MoVO structure by the heat treatment above 550 °C. V was removed from the specific structural site in MoVO since the lattice parameters and IR absorptions for the structural framework of MoVO changed by its removal. HAADF-STEM measurements implied the disordering of the metals adjacent to the V site in the hexagonal channel of MoVO in MoVO-600. Based on the results obtained above, we concluded that the V site located at the hexagonal channel was removed by the heat treatment above 550 °C to form the VMo phase. Acid properties were changed by removing this V as evidenced by NH_3 adsorption TPD and IR, which might prevent NH_3 from undesired combustion to enhance the AN selectivity.

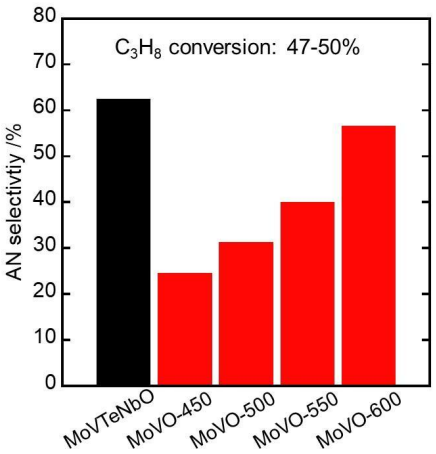

Figure 1. AN selectivity at the propane conversion of 47−50%.

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Disclosing the interaction between heterogeneous catalysts and substrates in liquid phase reactions

M. Stucchi[1*], F. Vasile[1], O. Serve[2], J.P. Korb[3], B. Vandegehuchte[2] and L. Prati[1]
[1]*University of Milan, Department of Chemistry, Milan, Italy*
[2]*TotalEnergies One Tech Belgium, Feluy, Belgium*
[3]*Sorbonne Université, CNRS, PHENIX, Paris, France*
[*]*marta.stucchi@unimi.it*

Keywords: NMR relaxometry, Carbon-based catalyst, 2D T1-T2 low-field NMR relaxometry, 13C high-field NMR, T1/T2 relaxation times, adsorption.

Introduction.
NMR relaxometry can be used to guide the understanding of a catalytic reaction [1]. In particular, high-field ^{13}C NMR analyses (400 MHz) allow measuring the relaxation time T1 of organic molecules in the presence of solvent. The ratio between $T1_{bulk}$ (molecule in solution) and $T1_{ads}$ (T1 measured in the presence of the catalyst) allows to quantify the strength of the interaction between the substrate and the catalyst, as the lower the $T1_{ads}/T1_{bulk}$ the higher the interaction. Considering the molecule-catalyst interaction one of the fundamental parameter of a catalytic cycle, the $T1_{ads}/T1_{bulk}$ ratio can be possibly correlated to the catalytic activity, importantly including the solvent as an active participant. However, such High-field NMR experiments allow collecting information only of local molecular dynamics. The variation of T1 is a proof of a preferred orientation, but an absence of a preferred orientation does not always mean that there is no interaction. Such limitation can be overcome by two-dimensional T1-T2 correlation spectra at low field NMR (20 MHz), where similar adsorption measurement, which are sensitive to the environment of the molecular probe, can prove the reality of the surface dynamics. So, ^{1}H Low-field NMR and ^{13}C High-Field NMR could be considered as complementary analyses to collect information of local molecular dynamics and on surface dynamics, returning a much more complete picture of the interaction that a molecule can have with the surface of a catalyst, which is crucial in defining the catalytic activity and selectivity.

Experimental/methodology.
In this work, the interaction of an aliphatic (n-octanal) and aromatic (benzaldehyde) aldehyde with a carbon based catalyst (Pd/C) has been studied by high-field and low-field NMR relaxometry, providing information about the different molecular motions on the catalyst surface. In particular, the solvent-effect (p-xylene) was explored. Moreover, all the experimental data have been compared to molecular modelling and to theoretical motions modelling [2].

Results and discussion.
Relaxation time ratio $T1_{ads}/T1_{bulk}$ in high-field NMR have been measured for benzaldehyde and n-octanal in p-xylene and in the presence or absence of Pd/C catalyst. The same molecules have been reacted in p-xylene with H_2 in the presence of catalyst showing a very different activity which was correlated with the different $T1_{ads}/T1_{bulk}$ ratio measured. Moreover, it could be also possible to demonstrate the fundamental role of the solvent. Then by parallel low-field NMR experiments and modelling we were able to qualify and quantify the affinity of the substrates with the catalytic surface. The interrelation of low-field and high-field NMR analyses finally allowed collecting information of local molecular dynamics and on surface dynamics, returning a remarkable and complete picture of the interaction of a molecule with a catalyst surface in the presence of solvent.

Acknowledgments
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Unraveling 1-Hexene Hydrogenation over Dilute Pd-in-Au Alloys

Jessi E.S. van der Hoeven[1,2,3,*], Hio Tong Ngan[4], George Yan[4], Joanna Aizenberg[2,3], Robert J. Madix[3], Philippe Sautet[4,5], Cynthia M. Friend[2,3]

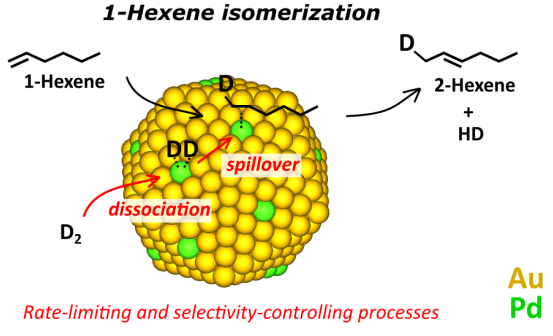
[1]*Materials Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, the Netherlands*
[2]*Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA*
[3]*Harvard John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA*
[4]*Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, CA 90095, United States*
[5]*Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095, United Stated*
[*]*j.e.s.vanderhoeven@uu.nl*

Keywords: bimetallic catalysts, hydrogenation, gold, palladium

Introduction: Dilute Pd-in-Au alloys are valuable materials for selectively hydrogenating alkynes and isomerizing alkenes [1,2,3]. By diluting Pd in a Au host, the selectivity towards semi-hydrogenated alkene isomers can be significantly enhanced and the unfavorable over-hydrogenation to alkanes suppressed. Yet, a detailed mechanistic study on the origin of the enhanced alkene selectivity over dilute alloy catalysts is still missing. Here, we combine experiment and theory to unravel the reaction mechanism, identifying rate-limiting and selectivity-controlling steps in 1-hexene hydrogenation over dilute Pd-in-Au catalysts [1].

Experimental/methodology: isotopically labelled 1-hexene hydrogenation experiments using D_2 were conducted under steady state conditions and at high 1-hexene conversion (92%) to gain insight in the reaction mechanism over the Pd_4Au_{96} and Pd catalysts. Quantitative analysis of all products and the number of deuterium atoms incorporated was achieved by simultaneously using an online mass spectrometer to monitor the HD formation, and a gas chromatography mass spectrometer to quantify the hexene and hexane products. Density functional theory calculations (DFT) were used to compute the free energy profiles for 1-hexene hydrogenation to n-hexane, and for isomerization to 2-hexene on a Pd atom in Au surface (Pd_1Au). Next, the reactivity and product selectivity of the calculated reaction mechanism for Pd_1Au was evaluated under operating temperature and pressure using microkinetic models.

Results and discussion: the isotope exchange hydrogenation experiments show that 1-hexene and hydrogen over a bimetallic Pd_4Au_{96} in silica catalyst preferentially form 1-hexene isomers, (trans&cis) 2- and 3-hexene, and only small amounts of hexane. The reaction is consistent with a Horiuti–Polanyi mechanism, similar to a mono-metallic Pd nanoparticle catalyst. Computation of the free energy profiles for 1-hexene hydrogenation and isomerization over a single Pd atom in a Au surface indicated that isomerization of 1-hexene to 2-hexene is energetically favorable due to the relatively large barrier for H_2 dissociation preventing hydrogenation to n-hexane. Microkinetic modeling established that H_2 dissociation on the single atom Pd sites, and H-spillover from these sites onto the Au host are rate-limiting and key in steering the selectivity of dilute Pd-in-Au alloys towards the hexene isomers. The mechanistic insights from this study contribute to the rational design of optimized dilute alloy catalysts for selective alkene isomerization.



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Comparison of mechanisms of deNOx and deN_2O processes on partial hydrated bimetallic Cu-Zn dimers in clinoptilolite zeolite - DFT study

I. Kurzydym[1], I. Czekaj[1*]

[1] *Department of Organic Chemistry and Technology, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Poland, Warszawska 24, 31-155 Cracow*
[*] *izabela.czekaj@pk.edu.pl*

Keywords: zeolites, deNOx, deN_2O, bimetallic, copper, zinc, DFT, SCR, clinoptilolite

Introduction. Nitrogen oxides (NOx) from human activities are a source of dangerous air pollutants such as acid rain and photochemical smog [1]. These pollutants are harmful to both human health and the environment. One of the more damaging nitrogen oxides is N_2O [2,3]. It is produced, for example, during nitric acid production or as a by-product of the NH_3-SCR process. As one of the greenhouse gases, it causes destruction of the ozone layer and its global warming potential (GWP) is approximately 310 times higher than the more famous gas CO_2. Currently, in plants where nitrogenous compounds are synthesised, the reduction of NO and N_2O takes place separately. In order to reduce costs, save space and time, a major problem is to find a catalyst that allows the simultaneous removal of these oxides [4].

Experimental/methodology. The ab initio density functional theory (DFT) method was used to calculate the electron structure of the presented clusters with StoBe software. The exchange and correlation functional was approximated with a Perdew-Burke-Ernzerhof (PBE) functional. It was used for the electron exchange and correlation. Milliken populations and Mayer's bond order factors were used to precisely analyse the electron structure of the clusters.

Results and discussion. The clinoptilolite zeolite with a Cu-Zn partially hydrated bimetallic dimer deposited was used as the catalyst in the study. Two variants were presented - an OH group on copper and an OH group on zinc.

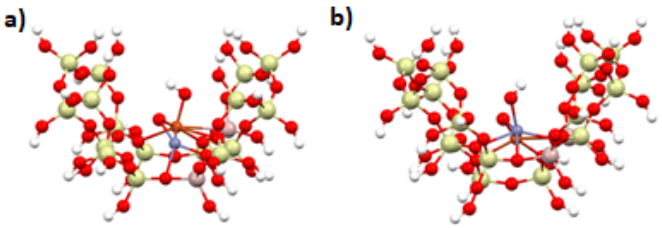

Figure 1. Cluster model of the clinoptilolite zeolite structure with deposited bimetallic dimer: a) Cu–O–Zn with OH group on Cu and b) Cu–O–Zn with OH group on Zn.

An analysis of the reaction mechanisms of the deNOx and deN_2O process was carried out. The energy differences between the stages of the process were presented. In addition, bond lengths and bond orders have been analysed to understand the nature of the systems in more detail. It was shown that, in the case of the deN_2O process, the order of the NO/N_2O molecules has a significant impact on the activation energies of the process. The different systems show similar efficiencies for both deNOx and deN_2O reactions. The adsorption energy of the OH group on the metal is important in this case - the OH group has a higher affinity for the zinc atom.

Acknowledgments
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Ab Initio Predictions for Heats of Adsorption and Reaction Barriers for Alkanes in Acidic Zeolites

F. Berger, M. Rybicki, J. Sauer*

Humboldt-Universität zu Berlin, Germany
**js@chemie.hu-berlin.de*

Introduction. Experimental kinetic studies deal with complex reaction networks, whereas computational studies can provide energy barriers, reaction energies, and pre-exponentials for individual reaction and adsorption steps. If made with sufficient, i.e. chemical, accuracy (± 4 kJ/mol), computational predictions are very useful to check critical steps in microkinetic models. Whereas the vast majority of kinetic experiments yield apparent enthalpy barriers, $H^{\ddagger}_{app}$, atomistic understanding and rationalization of the function of catalysts requires knowledge of intrinsic enthalpy barriers, $H^{\ddagger}_{intr}$. Therefore, adsorption enthalpies, H_{ads}, are needed to derive intrinsic enthalpy barriers from apparent barriers,

$$H^{\ddagger}_{intr} = H^{\ddagger}_{app} - H_{ads}, \quad (1)$$

but they are difficult to measure at reaction temperatures. In contrast, accurate computational methods can provide consistent adsorption enthalpies and intrinsic barriers at low and elevated temperatures. We propose an accurate quantum mechanical (QM) method that enables us to answer the long-standing question whether intrinsic activation enthalpies for alkane cracking depend on the alkane length or not.

Methodology. Our hybrid high level QM:low level QM method [1] has been demonstrated to yield chemical accuracy (4 kJ/mol for energies and one order of magnitude for rate constants) for the methylation of ethene, propene and butene in H-ZSM-5. Here, we combine density functional theory with some account of dispersion (DFT-D) as a low-level method for the full periodic structure and second-order Møller–Plesset perturbation theory (MP2) as a high-level method for cluster models to locally describe the molecule–surface interactions.

Results and Discussion. We apply this hybrid MP2:DFT-D approach in combination with molecular dynamics (MD) sampling (at the DFT-D level) to 19 cases of alkane adsorption in acidic zeolites with adsorbates ranging from methane to *n*-hexane and five zeolite models (H-MFI, H-CHA, and H-FAU) with low and high Si/Al ratios (2.6 to 23). The heats of adsorption show a mean absolute deviation from experiment of less than 2 kJ/mol.

The predicted heats of adsorption at reaction temperatures (650 K) support experimental results derived from spectroscopic measurements [2]. The Table shows that the observed decrease of experimental apparent barriers from propane to pentane for alkane cracking in MFI (28 kJ/mol) is largely due to increasing adsorption strengths (21 kJ/mol) and to a much smaller extent to decreasing intrinsic barriers (7 kJ/mol).

Alkanes in H-MFI (650 K): Experimental apparent activation enthalpies, $H^{\ddagger}_{app}$, calculated and experimental adsorption enthalpies, H_{ads}, as well intrinsic activation enthalpies, $H^{\ddagger}_{intr}$, purely based on experiments, Exp., or derived from experimental apparent barriers and calculated adsorption enthalpies, Calc., all in kJ/mol.

alkane	$H^{\ddagger}_{app}$	H_{ads}		$H^{\ddagger}_{intr}$	
	Exp.[2]	Exp.[2]	Calc.	Exp.[2]	Calc.
propane	146±4	−42±2	−43	189±2	189
butane	129±2	−51±4	−52	188±4	181
pentane	118±2	−65±1	−64	186±5	182
$C_5 - C_3$	−28	−23	−21	−3	−7

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Mechanism of CO-PROX Reaction over Mixed and Bare Cobalt Spinel Catalysts Revealed – DFT and isotopic investigations

F. Zasada[1], C. Hudy[1], K. Steenbakers[1], Z. Sojka[1],

[1]*Jagiellonian University, Kraków, Poland*
[*]*zasada@chemia.uj.edu.pl*

Introduction. Development of new efficient CO-PROX catalysts is mainly conditioned by an in-depth understanding of the reaction mechanism that governs the catalysts performance. One of the most attractive group of CO-PROX catalysts are spinels (AB_2O_4), which catalytic performance may be modified in the intended fashion upon careful selection of the A and B redox cations[1]. The guiding concept of these studies was to perturb the CO-PROX reaction progress by doping the parent cobalt spinel oxide (Co_3O_4) with foreign cations, and analyze the response of the isotopic CO_2 and H_2O profiles to the reaction temperature and catalyst selectivity getting insight into mechanistic details. The experiments have been confronted with DFT molecular modeling and first principle thermodynamics simulations.

Experimental: A series of mixed spinel oxide catalysts, $M_xCo_{3-x}O_4$ (M = Cr, Mn, Fe, Ni, Cu, and Zn), was synthesized via the combustion method, using nitrate precursors and then thoroughly characterized (XRF, XPS, XRD, IR, SEM). The catalytic tests were carried out in a gradient-less quartz reactor with a QMS spectrometer (Hidden) used for the detection of the diagnostic lines. For DFT modelling the spin unrestricted periodic-GGA+U DFT method with PW91 xc functional, implemented in the VASP package was used. The interaction of spinel planes with gaseous molecules of CO-PROX process at different conditions (T, p_x, x = CO, H_2, O_2, H_2O, CO_2) was accounted by first principles thermodynamics (FPT).

Results and discussion. It was shown that the predicted results can be reconciled with the experimental isotopic compositions of CO_2 and H_2O, and their evolution with the progression of the CO-PROX reaction only whith assumptionthat the suprafacial (Langmuir-Hinshelwood/Eley-Rideal, LH/ER) and intrafacial (Mars-van Krevelen, MvK) mechanisms operate concurrently. The essential features of the proposed fluctuating mechanism involve three main catalytic cycles, the relative participation of which depends on the catalyst nature and the reaction conditions[2]. Cycle I covers the indirect CO oxidation via suprafacial α–CO_3^{2-} and intrafacial β-CO_3^{2-} intermediates (LH/ER and MvK-LH/ER), whereas cycle II refers to direct CO oxidation into CO_2 by lattice oxygen (MvK). The last cycle (III) involves direct, unpreferable oxidation of hydrogen by adsorbed oxygen (LH/ER or EP).

In the revealed mechanism two types of carbonate adspecies are distinguished, depending on the adsorption locus (octahedral or tetrahedral cations). The carbonates attached to the dual Co^{tet}⌣Co^{oct} centers, are characterized by much higher energy of dissociation into $CO_{2(g)}$ than carbonates stabilized on the Co^{oct}⌣Co^{oct} pairs (ΔE = 1.29 eV and ΔE = 0.69 eV, respectively) and behave as spectators that being accumulated during the CO-PROX reaction are primarily observed in the IR spectra, but are rather of minor importance for the CO-PROX reaction. The Co^{oct}⌣Co^{oct} stabilized adspecies, in turn, are easily decomposed into $CO_{2(g)}$ thus act as interemdiates of CO-PROX. This observation resolves the contradictory claims about the mechanistic role of carbonates found in the literature[3]. The involvement of carbonate intermediates is directly confirmed by the established correlation between the selectivity and the relative content of $C^{18}O_2$ and $C^{16}O_2$ in the CO-PROX reaction products. The nascent Mars van Krevelen oxidation of direct CO oxidation into CO_2 is coupled with the subsequent LH/ER step, which is prompted by dissociative refilling of the oxygen vacancies by O_2, leading to the formation of O_{ads}.

Acknowledgments *This work was supported by the Polish National Science Center (NCN) Project OPUS-14, No 2017/27/B/ST4/ 01155.*

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Ab-initio study of Pd-based alloy catalysts for CO_2 hydrogenation to fuel

I. Kowalec[1], L. Kabalan[1], Z. Lu[1], C. R. A. Catlow*[,1,2,3], A. Logsdail*[,1]

[1] Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, United Kingdom
[2] UK Catalysis Hub, Research Complex at Harwell, RAL, Oxford, OX11 0FA, United Kingdom
[3] Department of Chemistry, University College London, London, WC1H 0AJ, United Kingdom
*Email: LogsdailA@cardiff.ac.uk, CatlowR@cardiff.ac.uk

Keywords: carbon dioxide, hydrogenation, *ab initio*, alloy catalyst, palladium, copper, zinc

Introduction:

Methanol synthesis by direct hydrogenation of CO_2 has been recognised as a potential route towards sustainable fuels for transport and a circular fuel economy.[1] The facilitation of direct CO_2 hydrogenation to methanol via a surface HCOO formate intermediate is crucial for desirable selectivity, as shown in the theoretical study of Cu catalysts by Medford *et al.*[2] Our previous work has shown that flat surfaces of a Pd catalyst have a high activation energy of initial CO_2 activation and hydrogenation to HCOO.[3] However, Pd-based catalysts supported on ZnO are potent catalysts for this reaction, with their reactivity attributed to the PdZn binary metallic phases.[4]

Methodology:

The reactivity of Tetragonal Body-Centred (TBC) PdZn (110) and (101) and Body-Centred Cubic (BCC) CuPd (110) alloy surface facets towards CO_2 activation and hydrogenation has been investigated computationally with comparison against low-index monometallic Face-Centred Cubic (FCC) Cu, Pd and Hexagonal Close-Packed (HCP) Zn surfaces. We used periodic DFT to ensure accurate representation of the metallic and alloy structures and catalytic processes, using the semi-local Bayesian error estimation density functional (mBEEF). [5, 6] All surface structures were verified against experimental observables. Transition states (TS) in the reaction pathway were investigated using NEB approaches to study the energy profile.

Results and discussions

CO_2 adsorption energy and activation energy of hydrogenation to the HCOO intermediate were calculated on Cu, Pd and Zn, CuPd and PdZn surfaces. The preferred starting CO_2 geometry was chemisorbed - a negatively charged and bent geometry, rather than physisorbed – a neutral and linear CO_2 geometry. [3] Chemisorption of CO_2 was exothermic on Pd (100) and Pd (110), and endothermic on Pd (111), Cu (100), (110), PdZn (101), (110) and CuPd (110) surfaces. The two largest TS energies were on surfaces that could only accommodate physisorbed CO_2, i.e., HCP Zn (0001) and FCC Cu (111). The results infer that metastable chemisorbed CO_2 intermediate facilitates further hydrogenation. The rate determining step varies across the metals where the surface with smallest TS energy is considered – for Cu it is CO_2 chemisorption, for Pd it is hydrogenation of chemisorbed CO_2, and for Zn it is hydrogen adsorption. In both investigated Pd-M (M = Cu, Zn) alloys, Pd is the more electronegative metal, and the surface atoms have a significant amount of negative charge from M. On Pd-M alloys CO_2 preferably binds *via* carbon to Pd and *via* oxygen to the Cu or Zn. CuPd shows a hydrogen adsorption energy between that of Cu and Pd metals, more stable CO_2 chemisorption, and a TS energy near that of Cu and Pd. Upon alloying Pd with Zn, the TS on PdZn (110) is reduced in energy below the net zero reaction energy, thereby highlighting the catalytic capability of this alloy. The study brings insight into rational design of modern $Cu_xPd_yZn_z$ alloy catalysts in CO_2 hydrogenation.

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Continuous oxidation of methane into methaol by N_2O over Cu-Zeolite: A combined experimental and theoretical study

Ning Liu, Biaohua Chen*, Ning Wang
Faculty of Enviroment and Life, Beijing, China (100124)
* chenbh@bjut.edu.cn

Keywords: Methane diretct oxidation to methanol, Zeolite, N_2O, reaction mechanism

Introduction. Methane (CH_4) transformation into methanol (CH_3OH) and its derivative (dimethyl ether, DME) has attracted great attentions due to growing production of natural gas by recently developed shale gas technology [1]. Direct oxidation of methane into methanol (DMTM) constituted a candidate, wherein the Cu modified zeolites [2] have shown promise in selectively converting CH_4 into CH_3OH under ambient conditions. Large amounts of works are mainly focused on CH_4-stepped-oxidation including steps of catalyst pre-oxidation (by O_2), CH_4 oxidation and CH_3OH extraction (by H_2O), which can hardly meat the demand of real chemical productions due to extremely low production capability (0-30) μmol g^{-1} catalyst h^{-1}. In this regard, developing continuous DMTM technique along with efficient catalyst is highly desirable.

Experimental/methodology. A series of Cu-, Fe-zeolites was prepared by wet-ion-exchange method. XRD, N_2-adsorption/desorption, H_2-TPR, UV-vis, XPS were employed to characterize the physiochemical properties of prepared samples. Continuous oxidation of CH_4 by N_2O was evaluated on a fixed bed reactor, under reaction conditions of GHSV of 12,000 h^{-1}, N_2O : CH_4 : H_2O ratio of 15 : 30 : 10 (balanced by He) and atmospheric pressure. The DFT, AIT and AIMD calculations were conducted based on the VASP and CP2K.

Results and discussion.

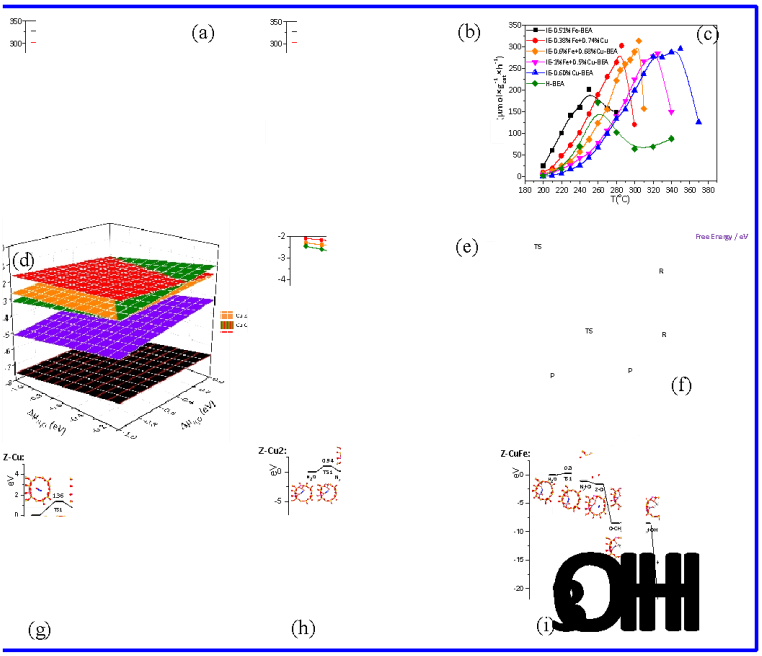

Fig. 1 (a-c) CH_3OH generation rate over series of Cu-, Cu-Fe-BEA zeolites; (d-e) active center stability evaluations by AIT; (f) free energy surface during AIMD simulation of H_2O-medieated proton transfer over [Cu-CH_3-Fe-OH]Z; (g-i) DFT mechanism simulation results over (Z-Cu), (Z-2Cu) and [Cu]+-[Fe]+ (Z-Cu-Fe).

Present work investigated continuous oxidation of CH_4, utilizing N_2O as oxidant, over a series of Cu-, Fe-zeolites (BEA, MFI, FER). The generation rate of the CH_3OH can reach as high as 300~2300 μmol g^{-1}catalyst h^{-1} CH_3OH. Excellent reaction stability was also verified by 70 h's long-term activity test. Finally, the mechanistic insight into the effects of H_2O as well as active center motifs were further studied by density functional theory (DFT) simulations, ab initio thermodynamics (AIT) and ab initio molecular dynamics (AIMD), based on which the reaction mechanism were well illustrated.

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Oxidative dehydrogenation of alcohols on gold: an experimental and computational study on the role of water and the alcohol chain length

L.Mastroianni[1,2*], T. Weckman[3], M. Di Serio[2], V. Russo[2], T. Salmi[1], K. Honkala[3], D. Yu. Murzin[1]

[1]*Åbo Akademi University, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Turku, Finland*
[2]*Università di Napoli 'Federico II', Department of Chemical Sciences, Napoli, Italy*
[3]*University of Jyväskylä, Department of Chemistry, Jyväskylä, Finland*
[*]*luca.mastroianni@abo.fi*

Introduction. Selective oxidation of primary alcohols to corresponding aldehydes plays a pivotal role in the modern chemical industry. The oxidation processes can be catalyzed by gold nanoparticles, but the critical issue is the nanoparticle size, which should be within few nanometers, because large gold particles are passive in catalysis. Concerning the structure sensitivity of gold in the selective oxidation of alcohols to aldehydes, conflictual results have been reported [1]. Lateral interactions on the catalyst surface might have a significant impact on the reaction energetics. Particularly, water has been suggested to play a prominent role in assisting oxidation processes [2]. In this work, the oxidation of primary alcohols promoted by gold nanoparticles was investigated both experimentally and computationally. The reaction kinetics and product distribution were determined in a microreactor for oxidative dehydrogenation of primary alcohols ranging from methanol to butanol. The effect of water was investigated by adding it to the reaction mixture in different amounts. The oxidation pathways were elucidated from a computational viewpoint on Au (111) surface to understand the role of water in elementary steps, thus proposing a plausible reaction mechanism for alcohol oxidation on gold nanoparticles.

Experimental/methodology. The microreactor device consisting of 10 plates with 9 parallel channels was coupled to an on-line gas chromatograph, equipped with a capillary column and a flame ionization detector. The gas flows were regulated with mass flow controllers and the alcohols were fed to the system with high precision pumps. The channels were coated with Au/Al_2O_3 catalyst prior to the experiments. Computational studies were performed using the Density Functional Theory (DFT) code GPAW [3].

Results and discussion. The observed reaction network comprised three parallel reactions, where the main reaction products were the aldehydes and ethers. The alcohol conversion was enhanced by the presence of water (Fig. 1a), which also resulted in an improved aldehyde selectivity (Fig. 1b).

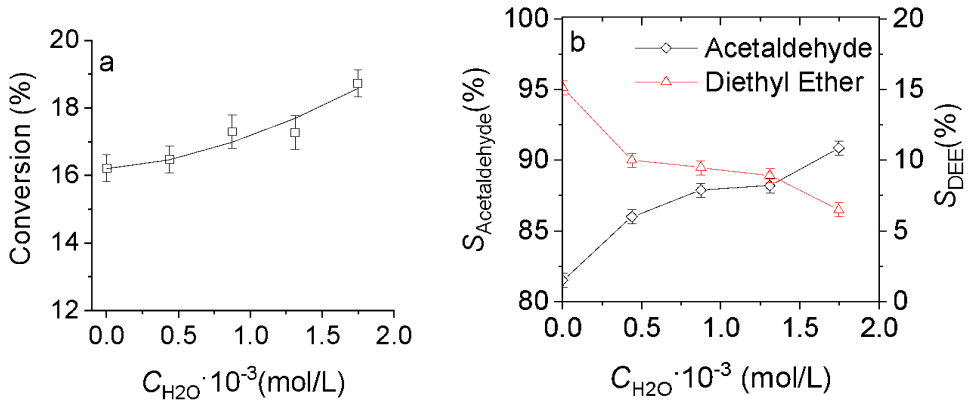

Figure 1. Ethanol oxidation over a gold on alumina catalyst in a microreactor at 250 °C: a) conversion and b) product distribution as a function of water concentration.

The DFT calculations proved that the oxygen dissociation is facilitated by the presence of water, thus supporting the experimental observations. Therefore, the combination of DFT calculations and experiments employed in this work was instrumental in revealing the role of water in alcohol oxidation on gold nanoparticles from the mechanistic viewpoint.

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Modelling the methanol to dimethyl ether reaction – coupling kinetic with transport from Å to cm scale

T. Fjermestad[1]*, R. Uglietti[2], D. Micale[2], M. Bracconi[2], A. Phan[3], A. Striolo[4,6], F. Iacoviello[5], S. Svelle[1], M. Maestri[2]

[1]*Center for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, Sem Sælands vei 26, 0371 Oslo, Norway*
[2]*Dipartimento di Energia, Politecnico di Milano, Via Lambruschini 4, 20156, Milano, Italy*
[3] *Department of Chemical and Process Engineering, University of Surrey, Guildford, Surrey, GU2 7XH, UK*
[4] *School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK 73019, USA*
[5] *Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, London WC1E 7JE, UK*
[6] *Department of Chemical Engineering, University College London, London WC1E 7JE, UK*
torstein.fjermestad@kjemi.uio.no

Keywords: Multiscale modelling, computational fluid dynamics (CFD), density functional theory (DFT)

Introduction. Understanding how the chemical kinetics is coupled to the transport processes in a catalytic reactor is an essential prerequisite for optimizing the performance of a catalytic reaction. The methanol-to-dimethyl ether reaction is catalyzed by the zeolite H-ZSM-5; and in this presentation, we apply multiscale modelling to investigate how the kinetics and transport processes depend on each other.

Experimental/methodology. A multiscale methodology[1] is used to couple the kinetics at the catalytic sites to the diffusion in the catalyst pellets and further to the gas flow in the reactor. The kinetics at the catalyst sites is computed using DFT calculations. A detailed pore structure of the catalyst pellet is obtained through X-ray tomography measurements. This pore structure is then used to simulate diffusion in the catalyst pellets. Finally, the gas flow in the reactor outside the catalyst pellets is obtained by use of CFD simulations.

Results and discussion. Figure 1 shows the average concentration of gas phase and average coverage of adsorbed species in a volume segment of length ΔZ = 0.0001 m placed at various positions along the reactor. The methanol-to-dimethyl ether reaction is fast indicated by the observation that the concentration of products has reached a constant level already 2 mm from the start of the catalyst bed.

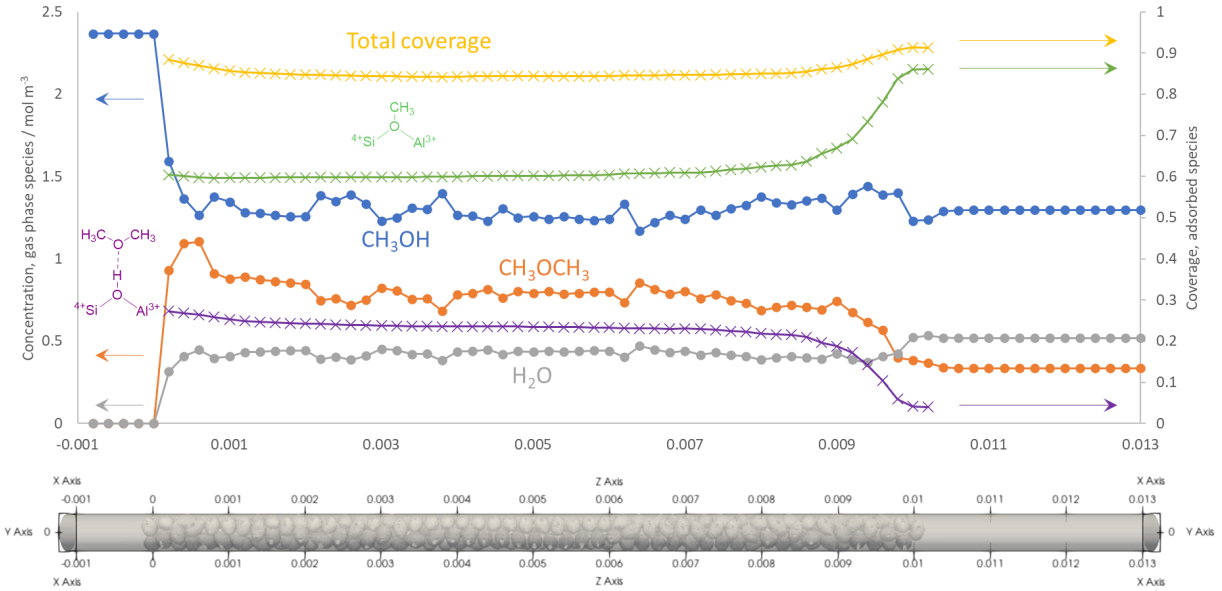

Figure 1. Concentration of gas phase species (filled circles, left axis) and coverage of adsorbed species (crosses, right axis) along the reactor. z = 0 m indicates the start of the catalyst bed.

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Continuous hydrogen production from liquid-phase formic acid dehydrogenation over Pd/AC catalyst: a modelling study

C. Martin*, A. Quintanilla, J.A. Casas

Departamento de Ingeniería Química, Universidad Autónoma de Madrid, Madrid, España
**celia.martinl@uam.es*

Keywords: hydrogen production, formic acid dehydrogenation, Pd/AC, kinetic modelling.

Introduction. The continuous generation of hydrogen by formic acid dehydrogenation (FAD) reaction at low temperature and in the absence of external additives is investigated in a fixed-bed reactor with the aim of providing a kinetic model that enables the further reactor desing. So far, significant progress has been done on the synthesis of heterogeneous catalysts, with the interest of producing CO-free hydrogen, and little on the chemical reaction engineering for the development of commercial technologies.

Experimental. A novel fixed-bed reactor configuration is proposed. A conductive β-SiC open-cell foam with high porosity (30PPI, supplied by SiCAT) is filled with a powdered commercial 10 wt.%Pd/AC catalyst (Noblyst® P1070, by Evonik). The FAD reactions were carried out up-flow at the following operating conditions: $C_{FA,0}$= 0.5-2 M, T= 25-55 ºC, W_{CAT}= 0.5 g, Q_L=0,125-1 mL min^{-1}, τ = 8.3-66.7 g_{CAT} h L^{-1} and using helium as a carrier gas (Q_G=17 mL min^{-1}). Gas samples were analyzed in a gas chromatograph (GC) while FA concentration in the liquid effluent was measured at 210 nm in a spectrophotometer.

Results and discussion. The FA concentration decreases by increasing the space time and reaction temperature (Fig 1a). It was found that the reaction follows a first order kinetic for FA. In general, the hydrogen flow rates measured by GC were lower than those calculated from the disapperared FA which indicates that some FA molecules or derivative from FA species remain on the catalyst surface without reacting, since hydrogen and CO_2 were the only gases detected in the gas stream. The kinetic parameters for both reactions, the FAD (r_1) and formation of FA -Pd catalyst species (r_2 of Scheme 1), were estimated.

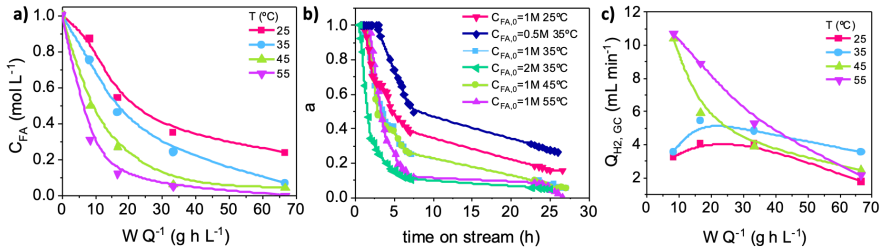

Figure 1. (a) Temporal FA concentration profiles and (b) catalytic activity *vs.* time on stream at $C_{FA,0}$= 0.5-2 M and T=25-55 ºC (c) hydrogen flow rates produced at $C_{FA,0}$= 1 M and T=25-55 C

The activity showed an exponential decay with the initial FA concentration and reaction temperature (Fig. 1b). According to these results, the elucidated kinetic model for the continuous production of hydrogen from FA is illustrated in Scheme 1.

$$\mathrm{FA} \xrightarrow{r_1} \mathrm{H_2} + \mathrm{CO_2}$$

$$\mathrm{FA} + \mathrm{catalyst} \xrightarrow{r_2} \mathrm{FA-catalyst}$$

$$(-r_{FA})_w = \left[k_1 \cdot \exp\left(-\frac{E_{a,1}}{RT}\right) \cdot C_{FA} + k_2 \cdot \exp\left(-\frac{E_{a,2}}{RT}\right) \cdot C_{CAT} \cdot C_{FA}\right] \cdot \exp\left(-k_d \cdot t\right)$$

$$(-r_{FA})_w \left(\frac{mol_{FA}}{g_{CAT} \cdot h}\right) = \left[9.87 \cdot 10^5 \cdot \exp\left(-\frac{53.6\ k\ mol^{-1}}{R \cdot T}\right) + 4.19 \cdot 10^4 \cdot \exp\left(-\frac{35.8\ kJ\ mol^{-1}}{R \cdot T}\right)\right] \cdot C_{FA} \cdot \exp\left(4.44 \cdot 10^2 \cdot \exp\left(-\frac{18.8}{RT}\right) \cdot C_{FA,0} \cdot t\right)$$

Scheme 1. Proposed kinetic model for the production of hydrogen from FA dehydrogenation

Noteworthy, the hydrogen flow rate profiles obtained (Fig. 1c) do not show the expected behavior. The hydrogen production decreases with the space time and is not influenced by temperatures above 35 ºC.

These results point out that the hydrogen mass transfer is controlling the catalytic performance. Therefore, the hydrogen production rate cannot be calculated from the FA reaction rate.

Improvement of Data and Metadata Quality in Catalysis Research: A Use Case Collection Methodology

N.Huskova[1], T.Petrenko[1], T. Boenisch[1]

[1]*High-Performance Computing Center Stuttgart University, Stuttgart, Germany*

The goal of the NFDI4Cat project is to establish a national research data infrastructure for catalysis research in Germany that ensures the data and metadata collected and shared by researchers are of high quality and adhere to established standards [1]. To achieve this goal, a comprehensive use case collection methodology has been developed. The methodology begins with the collection of use cases from researchers in the catalysis community through a dedicated platform. This platform includes detailed guidelines for the information required in submissions, ensuring that the use cases collected are relevant, accurate and complete. The collected use cases are then evaluated based on established criteria for data and metadata quality. Any identified issues are addressed through collaboration with the submitting researchers, to ensure that the use cases meet the required standards.

The collected use cases are then standardized what includes mapping the data and metadata to relevant ontologies and vocabularies, as well as ensuring consistency across different use cases. After standardization process is finished, information provided in use cases will be represented in RDF (Resource Description Framework) format and connected to the developed ontology. RDF is a standard format for representing data and linking it to ontologies, which allows for easy integration and cross-referencing of data [2]. The use of RDF and ontologies ensures that the data is machine-readable, linked, and can be easily integrated with other datasets, making it more discoverable and useful for the catalysis research community. Within the project, special attention is paid on the collection of use cases from different fields, including biocatalysis, homogeneous catalysis, and heterogeneous catalysis. This will provide a comprehensive representation of the field and allow researchers from different areas of catalysis to benefit from the collected use cases.

Proposed methodology serves as a valuable resource for the catalysis research community, promoting adherence to established standards and ensuring that the data and metadata shared by researchers are of high quality. It will help to facilitate data sharing and collaboration, as well as support the advancement of catalysis research [3].

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Breaking Barriers to Kinetic Modeling of CO_2 Hydrogenation to Hydrocarbons using Machine Learning

Aleksandr Fedorov*, Anna Perechodjuk, David Linke

Leibniz-Institut für Katalyse e.V, Rostock, Germany
**aleksandr.fedorov@catalysis.de*

Introduction. The kinetic modeling of heterogeneous catalytic reactions plays a key role in applied science and particularly in chemical engineering. The model development is usually based on using an expert's knowledge about reaction mechanism, rate-determining and equilibrium stages as well as solving the inverse task of kinetic. Modern machine learning (ML) methods can help and accelerate the development of such models. The key advantage of ML is that only the data is required for building regression models and, thus, we do not need to suggest (guess) reaction mechanism, rate-determining stages etc. However, the requirement of a lot of data for training and building reliable ML models limits so far their application for the small data. In the present work, we used ML for the kinetic modeling of a rather small dataset. To improve the generalization of ML models, we constrained the architecture of ML models by integrating the chemical and chemical engineering knowledge of the process. Our approach was developed and validated by carrying out a numerical experiment and finally applied for the kinetic modeling of experimental data using a challenging real-world problem, the CO_2 hydrogenation to higher hydrocarbons, as an example.

Figure 1. Molar flow parity plots of the obtained ML models: A, B – baseline and improved models from the nume rical experiments, respectively; C – im proved model describing the real data. D – conversion-selectivity plot.

Methodology and Experimental. For numerical experiments a plug-flow reactor model was developed using the kinetic model describing the CO_2 hydrogenation to hydrocarbons and suggested by Lucas Brübach et al. [1]. The small training dataset mimicking a typical kinetic experiment was generated and used for training ML models. Another lager test dataset was created for validating the ML models. To apply the suggested approach for real-world data, a Fe-K-Cu/Al_2O_3 catalyst was prepared by a wet-impregnation method and tested in CO_2 hydrogenation under various reaction conditions using a high-throughput setup.

Results and discussion. Figure 1 shows the generalization of the obtained ML models. The standard (baseline) ML model describes the training dataset correctly. However, its predicting ability is very low when we try to use this model for describing the whole test dataset (Figure 1A). It confirms the general consensus that ML requires a lot of data for building reliable models. But our improved model which was enhanced by integrating the chemistry knowledge describes training and test datasets correctly (Figure 1B). It is worth noting that reliable ML models could be even obtained in the case of noisy data. Finally, the suggested approach was succesfully applied for modeling CO_2 hydrogenation to hydrocarbons based on the experimental data (Figure 1C and 1D). The obtained model was shown to be able to describe reagent consumptions and product formations as well as parrafins, olefins, and alcohols distributions correctly. Thus, the suggested approach based on the intergating the chemistry knowledge into the architecture of ML models allows one to build reliable ML models using only a small data set as typical for experimental investigations. Therefore, our work significantly expands the scope of the application of ML for describing, analyzing and developing models of dynamic systems.

Acknowledgments
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Unsaturated dicarboxylic acid production from CO_2 and pyruvate with hybrid photo/bio catalytic system

M. Takeuchi[1*], M. Higashi[2], Y. Amao[1,2]

[1]*Graduate School of Science, Osaka Metropolitan University, Osaka, Japan*
[2]*Research Center for Artificial Photosynthesis (ReCAP), Osaka Metropolitan University, Osaka, Japan*
[*]*sg22081u@st.omu.ac.jp*

Keywords: Visible light driven process, Biocatalyst, CO_2 utilization, unsaturated dicarboxylic acid

Introduction.

Many plastic products used around the world for their high availability are synthesized from petroleum resources, and the large amount of CO_2 emissions during their production process and dependence on fossil fuels are serious problems. Based on this background, this research focused on fumarate, unsaturated dicarboxylic acid, that is a raw material for plastics such as polybutylene succinate having a good biodegradability, and unsaturated polyester resin with an excellent versatility and attempted to construct a visible-light driven fumarate synthesis system from CO_2 and biomass-derived substance, pyruvate. In a previous study, the synthesis of fumarate from carbon dioxide and pyruvate was achieved by a multi-enzyme system using malate dehydrogenase (MDH) and fumarase (FUM) [1], which have high substrate selectivity under mild conditions, while expensive NADH, the coenzyme of MDH sacrificially oxidized. Then, fumarate production system from CO_2 and pyruvate by connecting the multi-enzyme system to a photocatalytic NADH regeneration system consisting of triethanolamine (TEOA) as an electron donor, zinc meso-tetra (4-sulfonatophenyl) porphyrin (ZnTPPS) as a photosensitizer and [Cp*Rh (bpy) (H_2O)]$^{2+}$ (Cp* = pentamethylcyclopentadienyl, bpy = 2,2'-bipyridyl) as a catalyst[2] was invested in this study (**Fig. 1**).

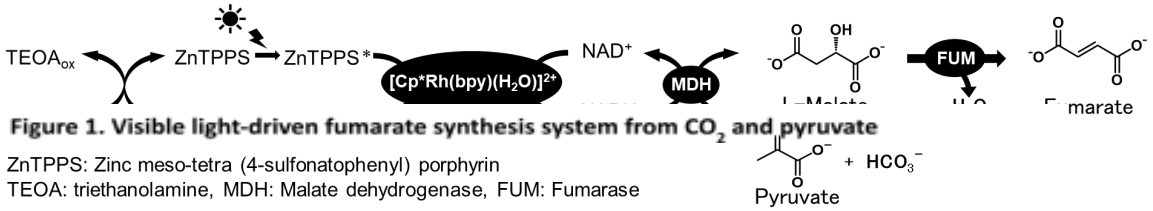

Figure 1. Visible light-driven fumarate synthesis system from CO_2 and pyruvate

ZnTPPS: Zinc meso-tetra (4-sulfonatophenyl) porphyrin
TEOA: triethanolamine, MDH: Malate dehydrogenase, FUM: Fumarase

Experimental/methodology.

The sample solution in HEPES-NaOH buffer pH 7.8 (5.0 mL) was consisted of sodium pyruvate (5.0 mM), $MgCl_2$ (5.0 mM), TEOA (0.2 M), ZnTPPS (10 μM), [Cp*Rh (bpy) (H_2O)]$^{2+}$ (10 μM), NAD^+ (0.5 mM), MDH (0.7 U) and FUM (0.5 U). After removing dissolved oxygen from the sample solution, the gas phase was replaced with CO_2. The reaction was started by irradiating 250 W halogen lamp as a visible light under at 30 degrees Celsius. The concentration of L-malate and fumarate production was determined by an ion chromatograph system.

Results and discussion.

Over the irradiation time, L-malate and fumarate increased steadily and the concentration of fumarate production was estimated to be 49 μM after 5 h irradiation (**Fig. 2**). The result shows that L-malate was provided from pyruvate and CO_2 gas using MDH and NADH regenerated by visible light irradiation, and the L-malate was dehydrated with FUM to provide fumarate.

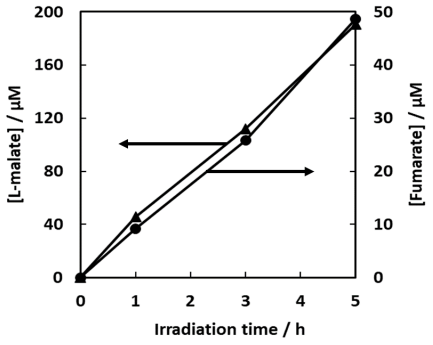

Figure 2. Time dependence of L-malate and fumarate concentration

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Mechanistic investigations at the alumina/water interface

J. Rey,[1] P. Clabaut[1], R. Réocreux[2], É. Girel[3,4], C. Michel[1]
[1]*Laboratoire de Chimie, Ens de Lyon, CNRS UMR 5182, Lyon 1, 69342 Lyon, France.*
[2]*Thomas Young Centre and Department of Chemical Engineering, University College London*
[3]*Direction Catalyse et Séparation, IFP Energies nouvelles, BP 3, 69360 Solaize, France.*
[4]*IRCELYON, CNRS UMR 5256, Lyon 1, 69626 Villeurbanne, France.*
*carine.michel@ens-lyon.fr

Keywords: alumina, stability, modelling, ab initio molecular dynamics, metadynamics

Introduction. γ-Al_2O_3 has remarkable properties as a support, but it is very sensitive to water. These structural changes can be retarded by the presence of polyols.[1] The mechanism of action of these additives is believed to lie in their chemisorption on the surface that would make γ-Al_2O_3 water-resistant[1]. However, little is known on which exposed facet(s) and what site(s) need to be particularly targeted for protection. The optimization of the structure of inhibitors is therefore a challenging task since the exact mechanism of the decomposition of γ-Al_2O_3 in liquid water remains unknown. We combine here experiments and theory to provide the atomistic mechanism for the early-stage decomposition of γ-Al_2O_3 in liquid water,[2] but also for the adsorption/desorption mechanism of (poly)-alcohols at the γ-Al_2O_3 / water interface.[3]

Experimental/methodology.

Experiments: A first alumina sample was obtained by calcination of commercial boehmite at 600 °C for 4 h. Three other shaped alumina were obtained: Fibers by precipitation of aluminum nitrate in an aqueous medium; Plates and Rods by a hydrothermal treatment of the first sample in water or in acidified water. Polyol adsorption isotherms were performed on the 4 samples using aqueous solutions of various polyols (0.5g.L^{-1} to 8g.L^{-1}) and the polyol concentration before and after adsorption was determined by HPLC.

Modeling. γ-Al_2O_3(110)/water interface was modeled performing *ab initio* molecular dynamics at the PBE-D3 level of theory using CP2K.[4] The reactivity at the interface is assessed by *ab initio* metadynamics.[2,3]

Results and discussion. Alumina samples containing particles with different shapes were exposed to a hydrothermal treatment in presence of various concentrations of polyol (sorbitol and xylitol). We determined the minimum surface coverage of polyol at which the decomposition of alumina gets inhibited, a quantity referred to as inhibiting coverage. Since this inhibiting coverage strongly correlates with the fractional area of the (110) facet of the alumina sample and only with this area, we concluded that the decomposition is initiated at the (110) facet. Then, performing *ab initio* metadynamics simulations, we probed the reactivity of this Al_2O_3(110)/water interface and identified specific aluminum tetrahedral centers that are particularly reactive with water. We showed that interfacial water molecules are involved in the mechanism, both as reactants for the hydration of aluminum and as intermediates for the proton reshuffling required by the decomposition mechanism. We managed to determine the barriers (all lower than 80kJ.mol^{-1}) for the 6 successive addition/elimination steps in a single simulation. Furthermore, the effect of xylitol was rationalized: its adsorption locally rendered the surface more hydrophobic and pushes water molecules away from the Al sites identified as water-sensitive.[2] Then, we investigated in details the adsorption/desorption mechanism of (poly)-alcohols at the γ-Al2O3 / water interface and found that liquid water induces a barrier of at least 20kJ.mol^{-1} due to the substitution of chemisorbed water and the solvent reorganization.[3]

Acknowledgments
This work is part of the "RatiOnAl Design for CATalysis" (ROAD4CAT) industrial chair, project IDEXLYON funded by the French National Research Agency (ANR-16-IDEX-0005).

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The role of polaronic states in the enhancement of CO oxidation by single-atom Pt/CeO_2

M. M. Kauppinen[1*], N. Daelman[2], N. Lopèz[2], K. Honkala[1]

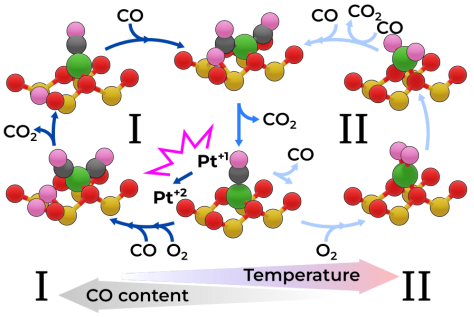
[1]*University of Jyväskylä, Jyväskylä, Finland*
[2]*Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain*
[*]*karoliina.honkala@jyu.fi*

Keywords: Single-atom catalysts, CO oxidation, Density Functional Theory, Microkinetic modeling

Introduction. Single Atom Catalysts (SACs) are a class of materials which maximize the utilization of noble metals by miniaturizing the active site down to a single metal atom.[2] SACs exhibit strong electronic coupling between the metal center and the host material. Thus, the electronic states of the metal form an ensemble, consisting of the ground and few metastable states [1], with metals in different oxidation states. The impact of dynamic oxidation states in reactivity for SACs towards, e.g. CO oxidation, are not fully understood. As these properties are difficult to study using experimental methods, computational studies can offer valuable insight.

Experimental/methodology. We present a Density Functional Theory (DFT) based Microkinetic model (MKM) that includes both ground and metastable states to address the reactivity of Pt_1/CeO_2 for CO oxidation. Electronic structure calculations were calculated with the Vienna Ab initio Simulation Package using the Perdew-Buke-Ernzerhof (PBE) functional and Hubbard correction with U_{eff}=4.5 eV applied to the 4f-orbitals of Ce. The MKM consists of a system of differential equations which were solved numerically using our own Python-based script. The simulations were carried out for a range of temperatures and different gas-phase compositions mimicking lean and very lean conditions.

Results and discussion.



Our DFT and MKM results together show that the reaction mechanism comprises two separate cyclic mechanisms. The cycles are sensitive to temperature, $CO:O_2$ ratio, and access to dynamic charge transfer. The apparent activation energy derived from our model is in agreement with experimental data in the literature. The agreement is only obtained if the dynamic oxidation state of the Pt center is accounted for in the microkinetic model. Based on our findings we suggest that samples with higher n-doping via oxygen depletion should be better in CO oxidation, as they help maintain the active state Pt^0 of the catalyst. This provides a general route to improve low-temperature oxidations at metal/oxide interfaces via charge transfer control.

Acknowledgments
This work was funded by the Spanish Ministry of Economy and Competitiveness, the Ministry of Science and Innovation, and Academy of Finland. The authors also thank the Barcelona Supercomputing Center (BSC-RES) for providing computational resources.

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Tuning the metathesis performance of a molybdenum oxide-based catalyst by silica support acidity modulation and high temperature pretreatment

Mariya Myradova[*1], Adam Węgrzynowicz[1], Adam Węgrzyniak[1],

Maciej Gierada[1], Przemysław Jodłowski[1], Joanna Łojewska[2], Jarosław Handzlik[2], Piotr Michorczyk[1]

[1]*Department of Organic Chemistry and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland.*

[2] *Department of Inorganic Chemistry, Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland.*

[*]*mariya.myradova@doktorant.pk.edu.pl*

Introduction.Light olefins are one of the most important intermediates in organic synthesis. The increasing demand for these chemicals, especially for propylene, drives propylene production for selective technologies, such as propane dehydrogenation or ethene and butenes metathesis.
Olefin metathesis is an important reaction of olefin disproportion, in which olefins are transformed into their homologues with longer or shorter carbon chains. Industrially used catalysts are silica-/alumina-supported molybdenum or tungsten oxides. Generally accepted mechanism (carbene mechanism) for supported MoO_x or WO_x catalyst assumes activation of C=C bonds in olefins into alkylidene intermediates (M=CHR, where M the metal atom, np. Mo or W, R —hydrogen atom or an alkyl group)-catalytically active species, which transforms upon further exposure to olefins yields into metathesis product and new alkylidene species. However, the number of alkylidene species on the surface of ill-defined catalysts usually does not exceed 2% [1]. Acid-base properties of catalysts support, post-synthesis catalyst modification, simple prior-reaction catalysts activation[2], and addition of organo-metallic compounds into the feed stream [3] or photoreduction with CO[4] have been found useful methods to tune the catalytic activity of the oxide-based catalyst.
This communication compares two approaches to activity enhancement of molybdena catalyst: by modification of acid properties of mesoporous silica support by Al-doping and by high-temperature pretreatment of silica-supported molybdenum catalyst in the flow of Ar, CO, H_2 and chosen alkanes.
Experimental/methodology.A series of Al-doped SiSBA-1 was obtained by post-synthesis silica treatment with ammonium hexafluoroaluminate as an external source of alumina. Obtained series was named AlSBA-1(x), where x-5, 15 and 30 stand for Si/Al molar ratio. Molybdenum oxide-based catalysts were obtained by the incipient-wetness impregnation method. The effect of pretreatment in the flow of Ar, CO, H_2, ethane and propane at 650°C was investigated on the $5MoO_x$ supported on pure SBA-1. The catalytic performance in propene metathesis at 50°C was measured by gas chromatography.
Results and discussion. It was found, that in comparison to conventional high-temperature pretreatment in inert gas or hydrogen, short pretreatment in hydrocarbon or carbon monoxide atmosphere significantly improves the catalytical activity of $5MoO_x$/SiSBA-1. Improvement in metathesis activity was also found in the case of Al doping of the silica support. However, with the increase in acidity, the decrease in selectivity to metathesis products was observed.

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Understanding the Acid Catalyzed Transformation of Biorenewable Lactones: Solvent Effects and Rational Design of Solvated Environment

Mohd. Ussama,[a] Gourav Shrivastav,[a] Rachit Khare,[c] Johannes A. Lercher[b,c] and M. Ali Haider[a]*

a Renewable Energy and Chemicals Laboratory, Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, Delhi, India

b Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, WA 99354, USA

c Department of Chemistry and Catalysis Research Institute, Technische Universität München, Lichtenbergstrasse 4, 85748 Garching, Germany

**haider@iitd.ac.in*

Introduction

Selective catalytic upgrading of biomass-derived feedstocks to fuels and chemicals is considered difficult owing to the complexity of the constituent's chemical structure and reaction environment. A firmly established strategy for the conversion of biomass-derived lactone molecules to useful chemicals involves the removal of oxygen-based functionalities via acid-catalyzed dehydrations. Differential stabilizations of the protonated transition state with respect to solvated protons are attributed to significantly causing higher reaction rates in polar aprotic solvents as compared to water. Taking insights from the relative stabilization of acidic protons in different solvents, mixtures of organic solvents with water are proposed, wherein on increasing the fraction of the organic phase, the aqueous phase is observed to preferentially cluster around the reactant with increased hydrogen bonding interactions. Moreover, acid-catalyzed reactions conducted in zeolites, also show an additional positive confinement effect, for which the steric stabilization of the transition state by the zeolite pores, leads to a drastic lowering of the activation energy. Ab-initio Molecular Dynamics (AIMD) simulations carried out in explicit solvent environments and have explained the reactivity of biomass-derived platform lactones in water and tetrahydrofuran (THF).

Methodology

AIMD-metadynamics implemented to predict the activation energy barrier and the reaction free energy for the acid-catalyzed dehydration reaction of MVL. Perdew–Burke–Ernzerhof (PBE) functional is used to calculate the electron exchange and correlation energies. Kohn–Sham orbitals are expanded using a short-ranged version of Gaussian-type double-ζ basis set optimized for the molecular system. The electronic density described using a norm-conserving Goedecker–Teter–Hutter pseudopotentials with a plane wave cut-off of 360Ry.

Results and Discussions

From the AIMD-metadynamics simulations, it is observed that in the solvated environment of water, a proton is forming stable hydronium ion clusters, whereas, in the case of THF, protonated reactant remains stable. The activation free energy barrier for the dehydration of MVL is observed to be higher by around 45 kJ/mol in water as compared to THF due to possible changes in the rate-determining step; C-H bond activation in water as compared to C-O bond activation in THF.

Intending to unravel the reactivity of MVL dehydration benefits from the confined pores of zeolite, MVL dehydration inside the BEA zeolite is performed in the gaseous phase (in the absence of solvents). The activity barrier for the MVL dehydration in the gaseous phase inside the zeolite drops off to 78 kJ/mol compared to the open solvation environment of water. For MVL dehydration inside zeolite in presence of water, the simulation is performed by occupying the zeolite pore with eight water molecules and MVL, preliminary results show higher reactivity barrier of dehydration in water compared to the gaseous phase inside zeolite.

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Green synthesis of DPA: catalyst screening and kinetic investigation.

F. Orabona[1,2], F. Taddeo[2], K. Eränen[1], W. Perez Sena[1], L. Verdolotti[3], M. Di Serio[2], D. Y. Murzin[1], T. Salmi[1], V. Russo[1,2].*

[1]*Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku/ Åbo*
[2]*Università degli Studi di Napoli Federico II, via Cintia, IT-80126 Napoli*
[3]*Institute of Polymers, Composites and Biomaterials, National Research Council, IT-80055 Portici, Napoli*

[*]*federica.orabona@abo.fi*

Introduction. The global concern on the depletion of fossil resources and their environmental impact is pushing the scientific community to shift from petroleum-based to sustainable chemicals. Diphenolic acid (DPA) is gaining much interest as a bio-based alternative to the toxic and endocrine-disruptor bisphenol A in the synthesis of epoxy resins, polycarbonates, and isocyanate-free polyurethanes. DPA is usually prepared by solvent-free condensation of phenol and levulinic acid in the presence of a homogeneous Brønsted acid catalyst [1]. Both levulinic acid and phenol are easily available and can be extracted from lignocellulosic biomass [2]. Mineral acids such as hydrochloric and sulfuric acid are traditionally employed as homogeneous catalysts; however, they are highly corrosive and require wastewater treatment. Therefore, heterogeneous catalysts provide a very attractive green alternative thanks to their high safety and facile separation from the reaction mixture. Electrophilic aromatic substitution of phenol occurs in ortho-para positions generating two stereoisomers, but *p*,*p*'-DPA has a higher commercial value as it strongly resembles the chemical structure of bisphenol A. Together with the DPA formation, esterification of levulinic acid might take place as a simultaneous side reaction. It is well-known that trans-esterification is usually slower than esterification in the presence of standard acid catalysts. Therefore, the kinetic probability to produce ester by-products is dramatically reduced when employing ethyl levulinate rather than levulinic acid as the starting molecule. Despite the afore-mentioned advantage, the reaction between ethyl levulinate and phenol has never been investigated until now.

Experimental/methodology. In this work, the synthesis of DPA was performed starting from both levulinic acid and ethyl levulinate as substrates. Sulfuric acid, zeolites as well as sulfonic acid resins were screened as catalysts. Very precise kinetic studies were conducted with the best catalysts in an isothermal and isobaric batch reactor by varying the reaction temperature, the reactant molar ratio, and the catalyst loading. The reaction products were identified by ^{1}H-NMR. The experimental data were used to derive rate expressions based on plausible catalytic reaction mechanisms. The kinetic model was combined with the batch reactor model consisting of ordinary differential equations (ODEs) to estimate the kinetic parameters by non-linear regression.

Results and discussion. The experiments revealed that the side reactions are suppressed when using ethyl levulinate as the reactant, showing a selectivity to *p*,*p*'-DPA close to unity for the first time. The catalyst screening revealed that the pore size of the heterogeneous catalyst plays a central role in the catalyst activity. The collected experimental results allowed a reliable quantification of the kinetic parameters. In future, the research will be focused on continuous operation in the presence of the best heterogeneous catalyst. The final goal is process intensification of the DPA production.

Acknowledgments
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Detecting Ketenes as Crucial Reactive Intermediates in Catalysis

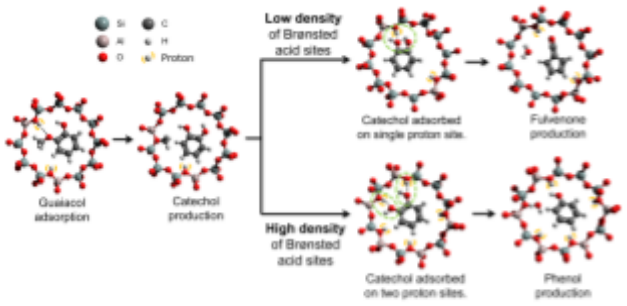
Patrick Hemberger*[1]
Paul Scherrer Institute, 5232 Villigen, Switzerland
**patrick.hemberger@psi.ch*

Keywords: ketene, reaction mechanisms, reactive intermediates, operando, photoelectron photoion coincidence, spectroscopy

Introduction. Thanks to their reactivity, ketenes, such as ethenone (H2=C=O), are very popular synthons in organic chemistry, as they can undergo a large variety of reactions. Ketenes can yield amides, carboxylic acids, esters and acid anhydrides, but are also utilized as reactants in cycloaddition reactions. Due to their high reactivity, they are impossible to detect using conventional chemical analysis tools such as GC/MS or NMR, however they were identified as crucial reaction intermediates in catalysis.[1]

Experimental/methodology. In the last decade a new online and operando detection technique was developed by coupling photoelectron photoion coincidence spectroscopy (PEPICO) and vacuum ultraviolet synchrotron radiation from the Swiss Light Source (SLS) to investigate reactive and elusive intermediates in catalysis.[2,3] PEPICO combines both mass spectrometry and photoelectron spectroscopy as a reaction microscope to explore mechanisms in heterogeneous catalysis. A nearly atmospheric pressure reactor is combined with a molecular beam sampling interface. Thanks to the rapid expansion into high vacuum reactive species exiting the reactor are preserved and, together with stable products, are directly detected and quantified.

Results and discussion. In this contribution we will focus on the role of ketene derivatives during lignin catalytic fast pyrolysis (CFP) and the methanol-to-olefin (MTO) process using zeolites: We will discuss how state-of-the-art PEPICO detection tools gained new insights into catalytic fast pyrolysis (CFP) of methoxyphenols as a function of the Brønsted acid site density. Guaiacol (2-methoxyphenol, Figure 1, left) is demethylated to catechol, to undergo either acid-catalyzed dehydroxylation to phenol or dehydration to the fulvenone ketene (c-C_5H_4=C=O). Fulvenone branches out and yields many products.[4] By increasing the Brønsted acid site density, catechol dehydration is inhibited by isolating the vicinal hydroxyl groups by surface coordination over the zeolite (see Figure 1). We found a five-fold phenol selectivity increase over high acidity faujasites.



Furthermore, we will discuss the role of ketene and its methylated analogues during the methanol-to-olefine process. Here, we synthesized ketene in-situ from methyl acetate and explored its reactivity over HSZM-5 zeolites. We find strong evidence that the ethenone (H_2C=C=O) is methylated on the catalyst surface to intermediately yield methyl ketene, which will rapidly decompose to ethylene as one of the first olefins during the MTO process. A second methylation gives rise to dimethyl ketene, which is the precursor of propene, after subsequent decarbonylation.[5]

Acknowledgments
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Esterification of levulinic acid catalysed with metal(IV) phosphates: An efficient route to obtain fuel aditives

G. Rocha[1*], F. Lopes[2]

[1]*Chemistry Department, University of Aveiro, Aveiro, Portugal*
[2]*Chemistry Department, University of Aveiro, Aveiro, Portugal*
[*]*grrocha@ua.pt*

Keywords: levulinic acid, metal(IV) phosphates, fuel aditives

Introduction. Fossil fuels still dominate the energy market. But, the depletion of fossil resources increased the search for renewable alternatives. Among several biomass-based chemicals, levulinic acid (LA) and levulinic esters (LEs) are important platform compounds with wide application, such as fuel additives. The esterification of LA and biomass derivatives can be easily performed if catalysed by different solid acids. The acidic nature of metal(IV) phosphates enclose all the characteristics to act as efficient solid catalysts[1,2].

Experimental/methodology. Our work started with the synthesis and characterization of the α- and γ-zirconium phosphates (α- and γ-ZrP). Then, the catalytic performance of these catalysts was evaluated in the esterification reactions of LA with ethanol (EtOH) using the conventional reflux method (CV). Different LA:EtOH molar ratios and catalyst:LA mass ratios were studied at 78°C during 6 hours. The best results were achieved with a LA:EtOH molar ratio of 1:20 and a γ-ZrP:LA mass ratio of 30% (Figure 1). Two products, 5-ethoxy-5-methyldihydrofuran-2-one (ethoxy-PL), an intermediate, and ethyl levulinate (EL) were formed. A blank reaction using the CV method was also performed with the former best conditions.
With the former best parameters, the esterification reactions of LA were performed by the microwave assisted method (MW) at 80°C and 100°C during 2 hours (Figure 1). Good results were obtained with the α- and γ-ZrP either at 80°C or 100°C. Blank reactions were also performed in the same conditions.

Given the good results obtained, the reactions performed by the MW with the α-ZrP at 100°C and γ-ZrP at 80°C were choosed to be monitored each half an hour (Figure 2).

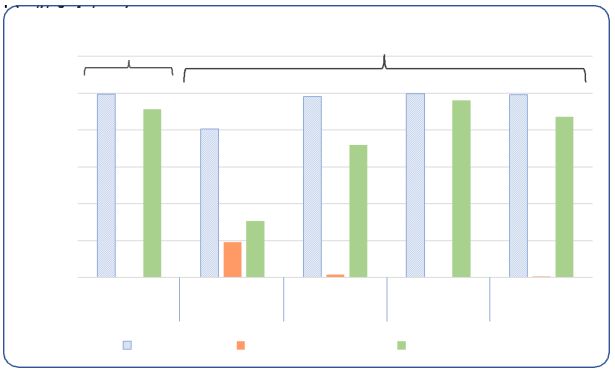

Figure 1

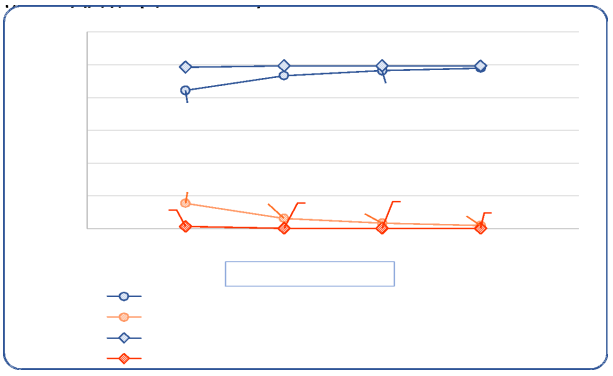

Figure 2

Results and discussion. The best LA conversions and EL selectivities were obtained with the MW after 2 hours of reaction either for the α-ZrP or γ-ZrP (Figure 1). These results are really good considering that the reaction time was substantially decreased from 6 to 2 hours, with both catalysts, which implies a considerable decrease in energy and water consumption. The results shown in Figure 2 are even more enlightening since it was verified that the monitored reactions start to give very good results even after 1 hour of reaction making our catalysts very promising in a near future.

The formation of the intermediate, ethoxy-PL, could compromise the formation of the EL in good yield. However, this step has been successfully overcome due to the perfect combination of several parameters (catalysts, molar ratio LA: EtOH, mass ratio catalyst:LA, temperature, time of reaction and method used).

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Approaching enzymatic catalysis with zeolites: an ab initio and experimental study of alkylaromatics competing reactions

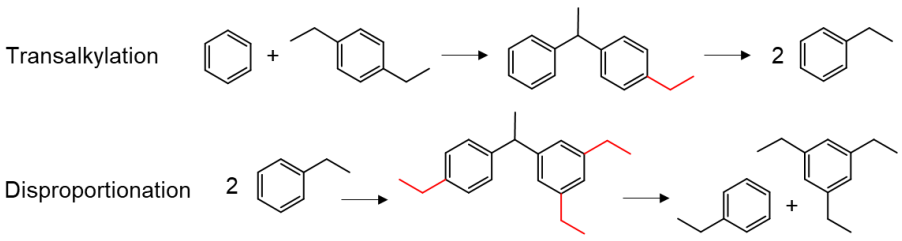
P. Ferri[1], C. Li,[1] M. Xie,[3] D. Schwalbe,[2] M. Moliner,[1] R. Gómez-Bombarelli,[2] A. Corma,[1] M. Boronat[1*]

[1]*Instituto de Tecnología Química, Universitat Politècnica de València - CSIC, Valencia, Spain*
[2] *Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, US*
[3] *Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, US*
[*]*boronat@itq.upv.es*

Introduction. Approaching the level of molecular recognition of enzymes with solid catalysts is a challenging goal, achieved in this work for the competing transalkylation and disproportionation of diethylbenzene catalysed by acid zeolites. The key diaryl intermediates for the two competing reactions only differ in the number of ethyl substituents in the aromatic rings, and therefore finding a selective zeolite able to recognize this subtle difference requires an accurate balance of the stabilization of reaction intermediates and transition states inside the zeolite microporous voids.[1,2] We present a computational methodology that combines a fast screeening based on force fields of all zeolite structures able to stabilize the key intermediates of potentially competing reactions with a more demanding periodic DFT study of the reaction mechanisms on the most promising catalyst candidates.[3,4] Then, the large pore zeolites with different microporous structure of channels and cavities proposed by the computational study have been synthesized, characterized and their catalytic activity tested.

Experimental/methodology. Force field (FF) calculations were performed with the GULP software and the Dreiding FF. The Density Functional Theory (DFT) gas phase mechanistic study was performed using the M062X functional and the 6-31g(d,p) basis set, as implemented in the Gaussian09 software. Periodic DFT calculations were performed with the VASP code, using the PBE-D3 funcional and PAW pseudo-potentials.

Results and discussion. From gas phase DFT mechanistic studies we identified the key diaryl intermediates involved in transalkylation and disproportionation reactions. Using the OSDB database[5] and FF calculations we selected the fifty zeolite structures that better stabilize the two identified diaryl intermediates. The mechanisms were then recalculated with periodic DFT inside the micropores of the twelve most promising zeolite structures, which were synthesized and tested. The experimentally observed selectivity in each zeolite correlates with the relative stability of the diaryl intermediates involved in both reactions, while the catalytic activity or reaction rate correlates with the calculated activation energy for the rate determining step of the most favourable pathway. Altogether, the internal architecture of the IWV zeolite is the best suited to enhance the transalkylation of diethylbenzene with benzene.



Acknowledgments

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The Role of Metal in the Anaerobic and Selective Regeneration of NAD^+

Jianwei Li[1], Joseph W. Burnett[1], Claudia Martinez Macias[1], Russell F. Howe[2], and Xiaodong Wang*[1]

[1]*Chemical Engineering, School of Engineering, Lancaster University, Lancaster LA1 4YW, United Kingdom*
[2]*Chemistry Department, University of Aberdeen, Aberdeen AB24 3UE, United Kingdom*
[*]*Corresponding Author: xiaodong.wang@lancaster.ac.uk*

Introduction. Biocatalytic redox reactions provide a useful tool for selective chemical synthesis and have been widely applied to industrial processes due their high rate of reactions, chiral selectivity, and mild conditions. Oxidoreductases have shown be able to oxidise target substrates such as alcohols, aldehydes or carboxylic acids for pharmaceutical applications using cofactor NAD^+ **[1]**. But NAD^+ is significantly expensive and is consumed in these reactions (forming NADH). Therefore, developing processes that can efficiently oxidise NADH into NAD^+, namely regeneration, is important. However, the regeneration reaction has hardly been reported using supported metal catalysts. For the first time, a group of monometallic catalysts comprising Pt, Pd, Au, Ni, Cu and Co supported on non-conductive SiO_2 have been examined, with the role of metal revealed. Very surprisingly, with its capacity of donating electrons, NADH has effectively made a thermal/heterogeneous catalytic process "electrocatalytic", governed by the hydrogen evolution reactions.
Experimental/methodology. The catalysts (1 wt.%) were prepared by wet impregnation and reduced for 1 h in H_2 at 400°C (except Ni at 500°C). The catalysts were characterized by chemical analysis, TPR, XRD, TEM, BET and pore size analysis and XPS. Details on the characterisation procedures, reaction setup and analytical methods are available in our previous report **[2]**.
Results and discussion. All catalysts showed similar distributions of metal particle size and mean particle diameters of around 4 nm, and nitrogen adsorption/desorption showed negligible pore blockage of the SBA-15 following addition of metal. The data shown in **Fig. 1a** are NADH conversions after 1 hour of reaction at pH 7. As illustrated, only SBA-15 supported Pt, Pd and Cu give NADH conversions significantly higher than that seen in the absence of catalyst. **Fig. 1b** shows time dependence of the UV-VIS spectrum during NADH conversion over Pt/SBA-15 at pH 7. The decreasing absorbance at 340 nm due to the nicotinamide ring is not accompanied by any change at 290 nm, indicating that the undesired NADH decay reaction **[3]** does not occur in the presence of the heterogeneous catalyst. **Fig. 1c** plots NADH concentration versus time at three different pHs. Clearly, an acidic environment gave the highest conversion (i.e., 80% at pH 5, 30% at pH 7 and 15% at pH 9). The obvious promoting effect of acidic conditions indicates the participation of H^+ in the regeneration reaction. The selectivity of the NADH conversion to NAD^+ was determined by enzymatic assay as close to 100%. The order of turnover frequencies (Pt >> Pd > Cu > Au, Ni and Co) coincides with those otherwise observed in electrochemical hydrogen evolution reactions. This has revealed that NADH can convert the metal sites into a "cathode" without an external potential and the NADH to NAD^+ reaction involves transferring electron and hydrogen atom separately. The catalytic mechanism (**Fig. 1d**) will also be elucidated (i.e., path b is the plausible one) in the presentation.

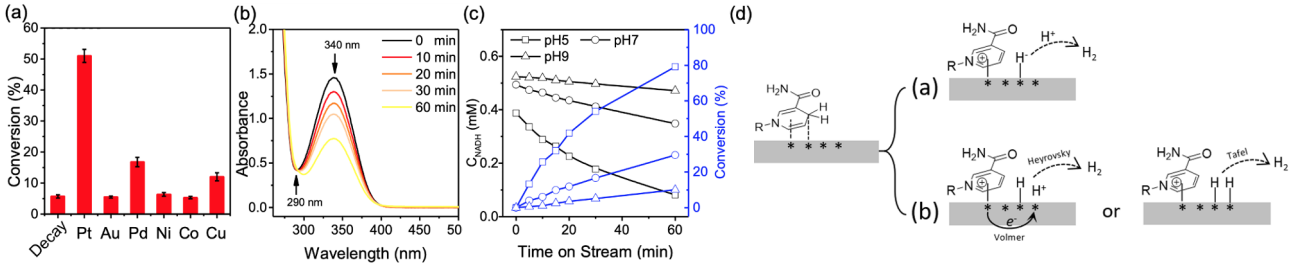

Fig. 1. NADH conversions over different supported metals (a), UV-VIS spectrum scans over Pt/SBA-15 (b), temporal NADH concentration and conversion at different pH over Pt/SBA-15 (c), plausible reaction pathway (d). Reaction conditions: 37°C, 0.5 mM NADH, pH 7 (for a, b), 100 ml min^{-1} N_2, 1 h, 60 mg (a, b) or 30 mg (c) of catalyst.

Acknowledgments. *This work was supported by the EPSRC New Horizons grants (EP/V048635/1 and EP/X018172/1).*

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Achieved Deuterated Difluoromethanethiolation of Aldehydes via Deuterated Benzenesulfonothioic Acid, Difluoromethyl Ester by Visible Light Catalysis

Chunyang Hu[1], Wenbin Yi[1,2*]

[1]*Nanjing University of Science and Technology, Nanjing, P.R. China*
[2]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute Organic Chemistry, Chinese Academy of Sciences, Shanghai, P.R. China*
[*]*Corresponding Author's E-mail : yiwb@njust.edu.cn*

Keywords: Photocatalytic; Deuteration; Radical; Deuteriodifluoromethylthiolation.

Introduction. Deuteration has been used in a wide range of applications such as organic synthesis, drug metabolism, nuclear magnetic resonance analysis and drug development. The incorporation of a fluorinated group into a molecule often alters its physicochemical properties and biological activity. In recent years, difluoromethanethiolated molecules have attracted a great deal of interest. We have developed a new SCF_2D-reagent deuterated benzenesulfonothioic acid, difluoromethyl ester ($PhSO_2SCF_2D$). And the introduction of the "SCF_2D" group into the aldehyde substrate by photocatalytic means.

Experimental/methodology. Adding aldehyde (0.5 mmol), $PhSO_2SCF_2D$ (1.2 equiv, 135 mg), $Ir(dF(CF_3)(ppy))_2(dtbbpy)PF_6$ (1.5 mol%, 8.4 mg), K_2CO_3 (0.25 equiv, 17.3 mg), anhydrous MeCN (4 mL) is added to the reaction tube (the feeding process is operated in a glove box). The reaction tube was placed in 10 W blue LEDs (455nm) at room temperature for 12-20 hours. The reaction solution was concentrated by a rotary evaporator, and products was separated by a chromatographic column.

Results and discussion. We investigated the scope of the transformation with respect to the aldehydes. In general, benzaldehyde with electron groups are converted smoothly into the desired product in high yields (76-87% yield). Benzaldehydes containing hydroxyl substituents are less reactive and therefore require longer reaction times (29-41% yield). At the same time, aliphatic aldehydes can be successfully applied in this scheme (66-81% yield). Moderate yields were obtained in the case of heterocyclic aldehydes (49-57% yield). SCF2D was also introduced into several complex aldehydes and the desired products were synthesised in moderate yields(47-53% yield).

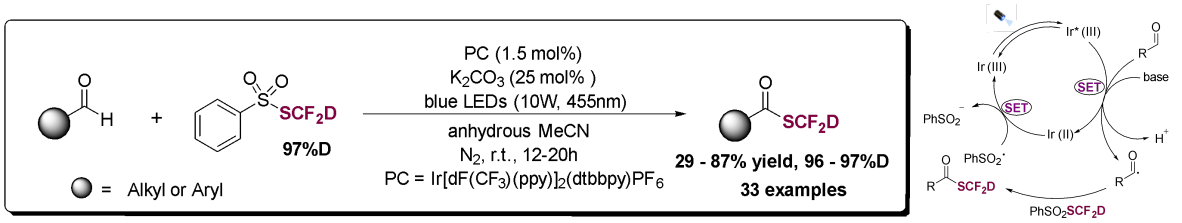

Figure 1. Deuterated difluoromethanethiolation of aldehydes

Acknowledgments

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Lifetime enhancement of methanol-to-olefins process via formaldehyde elimination over Ca species

Jinsong Luo[1], Tianci xiao[1], Chengyuan Liu[1*], Yang Pan[1*]

[1] *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, China*
[*] *lcy2012@ustc.edu.cn; panyang@ustc.edu.cn*

Introduction. Ca-modification has been identified to be effective in promoting propylene selectivity as well as catalyst lifetime during methanol to olefins (MTO) process. Recently we found that increasing Ca loading has caused a surge of H_2 and CO in the effluent accompanied by a plunge in aromatics yield. We proved that formaldehyde (HCHO) elimination of over CaO species accounts for this phenomenon and its role during MTO process was systematically studied.

Experimental/methodology. To suppress secondary reactions, a home-made low pressure catalytic reactor was employed, which combined with in situ synchrotron radiation photoionization mass spectrometry (SR-PIMS) allows the unambiguous detection of intermediately generated HCHO [1].

Results and discussion. Ca-modified ZSM-5 exhibited higher yield of olefins (Figure 1a) during the methanol to olefins (MTO) process. The FT-IR spectra of pyridine adsorbed indicated a reduced Brønsted acid site (BAS) concentration after Ca-modification, which would hinder consecutive reactions of olefins to form aromatic species and thus contributing to lifetime enhancement and promotion of olefin-based cycle [2]. Interestingly, unusual high CO and H_2 concentration in the effluent was observed for the Ca-modified samples (Figure 1b), which is accompanied by a decrease in aromatics yield. Such phenomenon is more prominent for samples treated via impregnation method, which introduces much more CaO species compared with those treated via ion exchange method. Further evidence was provided by CO_2-TPD, for samples treated via impregnation show higher basicity compared with the one treated with ion exchange method, indicative of higher CaO content. Several metal oxides have been identified to be efficient in decomposing HCHO during MTO process in some previous works [3-4], which triggered our interest into investigating the role of CaO.

Physically mixing HZSM-5 with CaO has also led to enhanced lifetime and the obvious decrease of HCHO was observed (Figure 1c) using PIMS method. The decrease of HCHO yield was accompanied by the decreased yields of butadiene and aromatic species, since HCHO acts as crucial intermediate that involves in the formation of dienes and aromatics. Therefore, the olefin-based cycle was favored via HCHO elimination, leading to higher propylene yield. The mechanistic insight into CaO species supplemented the understanding of Ca-modified HZSM-5, providing guidance for catalyst design of MTO process.

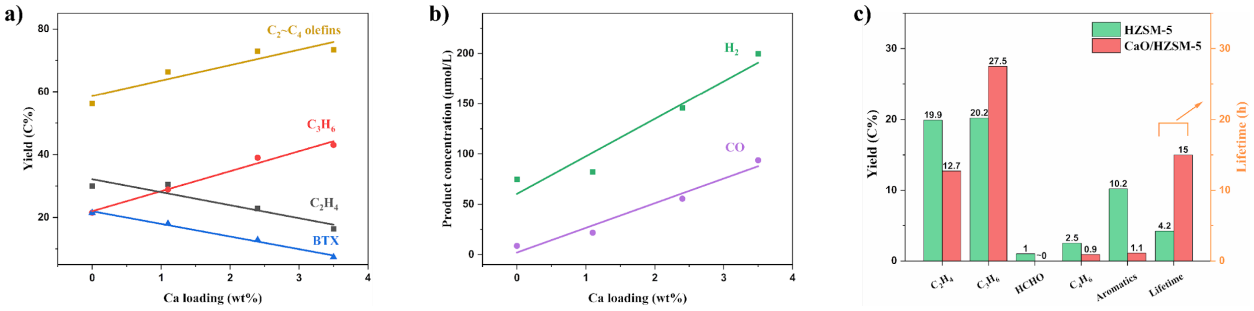

Figure 1. Yield of main products (a) and product concentration of H_2 and CO versus Ca loading (b). Yield of main products and lifetime for HZSM-5 and CaO/HZSM-5 (c).

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Palladium-catalyzed allylation of *N*-CF_3 secondary amines

Leibing Wang,[1] Wenbin Yi[1*]

[1]Nanjing *University of Science and Technology, Nanjing, P.R. China*
[*]*Corresponding Author's E-mail: yiwb@njust.edu.cn*

Keywords: Palladium Catalysis, *N*-CF_3 Secondary Amines, Allylbenzene.

Introduction. Recently, the synthesis of *N*-CF_3 derivatives has attracted more and more attention because of the role of trifluoromethyl in changing the lipophilicity, conformation, membrane permeability and enhancing the metabolic stability of the parent molecule. *N*-CF_3 secondary amines (R-$NHCF_3$) are excellent precursors for the construction of *N*-CF_3 derivatives, but due to the strong electron-withdrawing and steric bulk of trifluoromethyl moiety, their N-H bonds are more inert compared to the non-alpha-fluoro-substituted amines. In addition, the easy elimination of hydrogen fluoride by *N*-CF_3 secondary amines also makes it difficult to be exploited. Therefore, it is highly imperative to develop derivative reactions of *N*-CF_3 secondary amines with catalytic systems, which will fill the research gap of R-$NHCF_3$ catalytic reactions. In this study, *N*-CF_3 allyl compounds were synthesized by the palladium-catalyzed system.

Experimental/methodology. Under nitrogen atmosphere, a 10 mL Schlenk flask equipped with a magnetic stir bar was charged with the *N*-CF_3 secondary amine (0.5 mmol), palladium chloride (0.05 mmol, 0.1 equiv.), allylbenzene (0.75 mmol, 1.5 equiv.), dimethyl benzoquinone (0.75 mmol, 1.5 equiv.) and dry DMSO (1.5 mL). The mixture was stirred at 100℃. After 18 h, the reaction mixture was cooled to rt. The crude mixture was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using the indicated solvent system to give the corresponding products.

Results and discussion. In this work, we successfully coupled with *N*-CF_3 secondary amines with the assistance of palladium chloride/dimethyl sulfoxide catalyzed allylic C-H activation to obtain novel products. Under standard reaction conditions, the range for the preparation of *N*-CF_3 cinnamic compounds from *N*-CF_3 secondary amines was investigated. Taking allylbenzene as the olefin substrate, we found that it is compatible with electron-rich or electron-deficient aromatic amines as well as a wide range of functional groups. The respective yields are influenced by electron effect. The secondary amines with strong electron-withdrawing groups (cyano, trifluoromethyl) were transformed to products in moderate yields (55% and 60%). In contrast, substrates with strong electron-donating group (methoxy) were obtained in lower yields (28% and 31%). Halogen atoms on the aromatic ring including fluoro and iodo could be well compatible. It is worth to mention that aliphatic *N*-CF_3 secondary amines are poorly tolerated (13%-18%), most probably because of their worse stability.

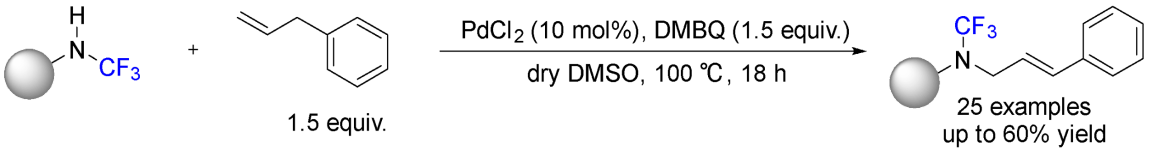

Figure 1. The preparation of *N*-CF_3 cinnamic compounds from *N*-CF_3 secondary amines

Acknowledgments

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Role of formaldehyde in promoting aromatic selectivity during methanol conversion over gallium-modified zeolites

Tianci Xiao[1], Wu Wen[1], Chengyuan Liu [1*], Yang Pan [1*]

[1]*National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, China*
[*] *lcy2012@ustc.edu.cn; panyang@ustc.edu.cn*

Introduction. We proposed that formaldehyde (HCHO) derived from the direct dehydrogenation of methanol over gallium species in HZSM-5 zeolite, promoted aromatic selectivity during methanol conversion through a HCHO-induced aromatic formation pathway[1].

Experimental/methodology. To capture the intermediately generated formaldehyde, an in situ low-pressure catalytic reactor combined with in situ synchrotron radiation photoionization mass spectrometry (SR-PIMS) was employed to perform the catalytic conversion of methanol[2].

Results and discussion. We found that formaldehyde (HCHO) was remarkably boosted over Ga-impregnated HZSM-5, along with the enhanced selectivity to aromatics. The higher Ga loadings, the higher productions of HCHO and aromatics (Fig. 1a). After eliminating HCHO into CO and H_2 by physically mixing Y_2O_3 with Ga-impregnated HZSM-5, aromatic production decreased to the level of parent HZSM-5. It indicated that there existed a new pathway to generate aromatics involving formaldehyde participation, which is called as HCHO-induced aromatic formation pathway. Previous works suggested that HCHO can react with olefins to form dienes via Prins reaction (HCHO + olefins ⟶ dienes + H_2O), and dienes react stepwise with HCHO to form H-poor products, aromatics and eventually cokes[3].

We verified that the direct dehydrogenation of methanol over Ga_2O_3 clusters contributed the more HCHO production. Cationic GaO^+ species had no activity to generate HCHO but promoted the dehydrogenative aromatization process of alkenes. In addition, an interesting phenomenon was observed in which the HCHO yield sharply increased after reduction-oxidation treatment of Ga-impregnated HZSM-5. It can be attributed to the migration of gallium from the external surface of the zeolite crystallites to their intracrystalline volume after reduction-oxidation treatment, leading to higher cationic GaO^+ concentration and redispersed Ga_2O_3 (Fig. 1b). Thus, both the LAS-induced and HCHO-induced aromatic formation pathways were enhanced, resulting in higher aromatic selectivity and faster deactivation. The above perspectives supplement the single LAS-induced aromatic formation mechanism with new insights into the HCHO-induced aromatic formation pathway over Ga-modified zeolites and provide a new thought to manipulate the MTH reaction.

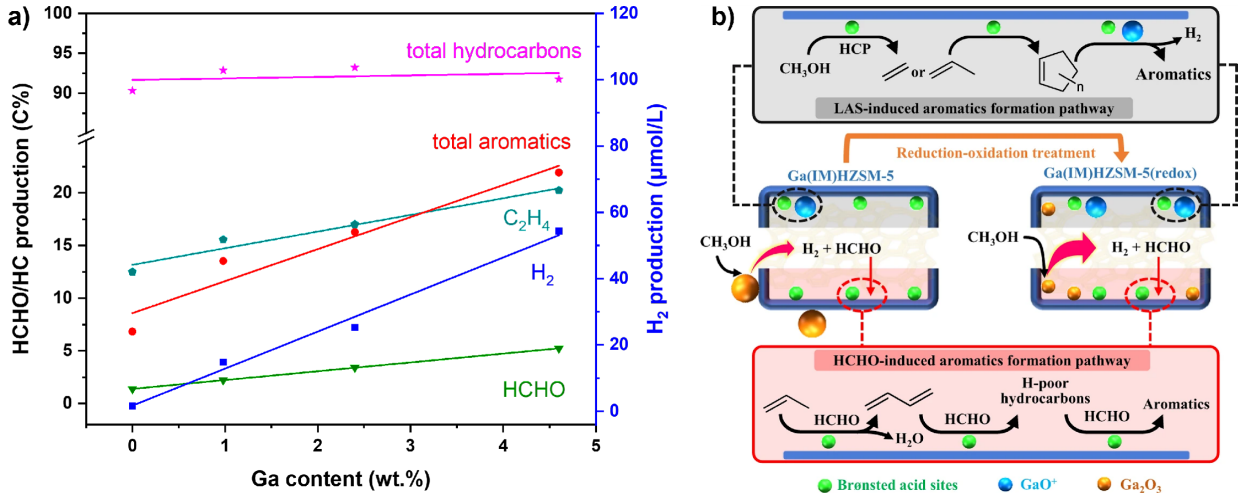

Fig 1. The production of HCHO, C_2H_4, total aromatics, total hydrocarbons and H_2 versus Ga content (a). Proposed evolution mechanisms of catalyst and aromatic formation (b).

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Copper-catalyzed peroxidation of cyclohexane in liquid phase: an elucidation of mechanism and cycle stability of Cu(I) and Cu(II) in tetradentate *N,N,N,N*-Cu complexes.

M. Abu Rasheed[1], E. Aunan[1], N. Cao[2], A. Nova[2], I. Gerz[1,3], R. J. Rama[1], M. Signorile[4], G. Deplano[4], S. Bordiga[4], U. Olsbye[1*].

[1]*Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, Sem Sælands vei 26, 0315 Oslo, Norway.*

[2]*Hylleraas Center for Quantum Molecular Sciences, Department of Chemistry, University of Oslo, Sem Sælands vei 26, 0315 Oslo, Norway.*

[3]*Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34–36, 45470 Mülheim an der Ruhr, Germany.*

[4]*Department of Chemistry and NIS Interdepartmental Center and INSTM reference center, University of Turin, via Pietro Giuria 7, I-10125 Turin, Italy.*

*unni.olsbye@kjemi.uio.no

Keywords: Cyclohexane oxidation, copper complex, catalysis, catalytic mechanism.

Introduction.

Due to the high dissociation energy of C–H bonds in saturated hydrocarbons, harsh conditions are required to oxidize this bond. However, the economic importance of this conversion for both chemical industry and environmental aims has led to extensive research to address the activation of C–H bonds under mild conditions (room temperature and ambient pressure) using catalysis.[1,2]

To this end, we are developing copper-based homogeneous and heterogeneous systems as catalysts for the oxidation of alkanes.[3] These systems were inspired by metallo-enzymes belonging to the pMMO (particulate methane monooxygenase) and LPMO (lytic polysaccharide monooxygenase) families in bioorganism. They oxidize methane and polysaccharides, respectively, into corresponding oxygenated species with high turnover rates.[4–7]

In this study, the peroxidative oxidation of cyclohexane to the corresponding alcohol and ketone over selected tetradentate *N,N,N,N*-Cu complexes was investigated.[3] The substrate cyclohexane offers a symmetric source of C–H bonds and is of paramount importance as precursor for adipic acid and nylon production.[8,9]

Experimental/methodology.

Catalytic tests were performed in closed vials as well as in a high-pressure PARR reactor. GC-MS was utilized to analyze samples at different time intervals after applying work-up steps, along with a parallel NMR in-situ analysis to establish the mass-balance. Reactivity of Cu(I) and Cu(II) initial oxidation states were compared and screened over different reaction conditions. Computational studies were performed to establish a reaction cycle corresponding to the experimental results. This model was further supported by UV-Vis and XAS studies.

Results and discussion.

NMR analysis showed mass-balance of 98 ± 0.03 % during the first 4 h, suggesting high selectivity to alcohol/ketone without over-oxidation products. Testing results showed higher reactivity when the Cu(I) complex is used. UV-Vis analysis of the reaction mixture at different time intervals revealed some interesting features. A change in catalyst resting state, from Cu(I) to Cu(II), was observed with time on stream, indicative of a change in the catalytic system that alters the relative rates of Cu oxidation and reduction; respectively. This observation was corroborated by UV-VIS measurements, which showed a shift in the absorption frequency of the Cu(II) d-d transition band upon oxidation from the Cu(I) state during reaction, compared to the Cu(II) version of the parent complex. GC-MS and UV-Vis data also suggest a double-role of water in these systems, i.e.; as an catalyst activator, yet simultaneously a source of catalyst degradation. These findings were further supported by XAS measurments to investigate the mechanism as well as Cu(I)/Cu(II) cycle stability over time between the two complexes. Both experimental and computational studies suggest a redox Cu(I)/Cu(II) cycle during the first 4 hrs.

Acknowledgments

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Unraveling the reactivity of metastable active sites in methane dehydroaromatization

Iqra Ahangar[1], and M. Ali Haider[1*]

[1]*Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India*

**Corresponding authors: haider@iitd.ac.in*

Keywords: MDA, Mo/ZSM-5, metastable active sites, kinetics.

Introduction.

Molybdenum (Mo) impregnated on zeolite ZSM-5 is the most studied and promising bifunctional catalyst for directly transforming methane to aromatics in a non-oxidative environment. The molybdenum carbides formed during the progress of the reaction exhibit notable catalytic behavior in methane activation and formation of crucial intermediate [1]. The high-energy metastable Mo carbide structures are more reactive and play a vital role in cluster catalysis as numerous isomers of the cluster become accessible under different reaction atmospheres. This indicates the dynamic nature of the catalyst and suggests that the active site might not be just one. So, this gives an intuitive idea that at high temperatures, these metastable structures do all the turnovers [2]. In the present study, using the DFT studies, two different forms of Mo carbide having the same stoichiometric ratios of Mo: C anchored in the zeolite cage have been investigated to gain an insight into the mechanism of methane activation to the formation of possible intermediate for benzene formation. Furthermore, the Mars Krevelen type mechanism has been postulated in the MDA (methane dehydroaromatisation), considering direct ethene formation without undergoing ethane formation on both metastable and global minima carbide cluster active sites.

Experimental/methodology.

To investigate methane to C_2 conversion, we have utilized electronic structure methodology based on the Density Functional theory (DFT). The software package DMol3 code implemented in Material Studio program package 2020 (Biovia, San Diego) was used in the current study. Spin-polarized DFT calculations were performed to comprehend methane dehydrogenation to ethane, ethylene, and acetylene on a Mo_2C_6 cluster encapsulated in zeolite ZSM-5.

Results and discussion.

In the present work, the metastable and most stable Mo_2C_6 cluster was separately anchored on a single Al atom binding through only one Mo atom in 10 MR ring of ZSM-5. The first C-H bond of methane is activated on the metastable Mo carbide active site with a barrier of 72 kJ/mole, which is reduced by half what is observed in the most stable active site (133 kJ/mol). The active site for another methane is methyl metal. The second C-H bond is activated at a distance of 4.92 Å with an activation barrier comparatively higher than the first C-H activation. The C−H activation of ethylene (C_2H_4) to form vinyl (C_2H_3) and acetylene (C_2H_2) are found to be unfavorably owing to high activation barriers (103 kJ/mol and 125 kJ/mol, respectively). Ethane (C_2H_6) and ethyl (C_2H_5) dehydrogenation, having a considerably lower barrier of 81 kJ/mol and 90 kJ/mol, respectively, would be a preferred route; hence the acetylene formation is considered unlikely in this reaction mechanism. A similar trend was observed in the most stable molybdenum carbide active site. Haider and co-workers also demonstrated that the dehydrogenation of ethane to ethylene and further dehydrogenation to acetylene on bare Mo_2C_6 clusters is difficult [2]. It is not worth mentioning that these metastable active sites are equally helpful in C-H activation and C-C coupling. Furthermore, a possible alternative route for intermediate formation, considering the dynamic nature of the active site, has been explored using DFT simulations where the proposed pathway takes the carbon of the active site in intermediate formation.

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Performance of a Mn catalyst for the ozone oxidation of methyl ethyl ketone and by-products formation at room temperature

Hae-Young Ahn, Jin-Soo Jeon, JiHyeon Song
Department of Civil and Environmental Engineering, Sejong university, Seoul, South Korea

Keywords: Manganese oxide catalyst, Ozonation, Methyl ethyl ketone, By-products

Introduction.
Organic solvents used in gravure printing processes commonly contain high concentrations of methyl ethyl ketone (MEK). Ketones, such as MEK, are known to be difficult to remove by conventional adsorbents such as activayed carbon. Therefore, as an alternative, catalytic oxidation processes at room temperature have been studied and applied. This study was conducted to develop a pilot-scale system to oxidize MEK in the presence of ozone using a manganese oxide catalyst at room temperature and to determine ozone oxidation efficiencies and oxidation by-products.

Experimental/methodology.
Gamma alumina was selected as a support for the Mn catalyst. Manganese acetate ($(CH_3COO)_2Mn{\cdot}4H_2O$) was used to impregnate manganese on the surface of the support. The support was immersed in the Mn solution for 10 minutes, dried at 105°C for 2 hours, and calcinated at 800°C for 6 hours. A cylindrical column was filled with 50 mL of the ozone-active Mn catalyst at room temperature, and an air stream mixed with MEK at the inlet concentration of 500 ± 50 ppm was continuously introduced at a gas hourly space velocity (GHSV) of 18,000 hr^{-1}. The ozone oxidation of MEK is $C_4H_8O + 11O_3 \rightarrow 4CO_2 + 4H_2O + 11O_2$, and the stoichiometric O_3/MEK ratio is 11:1 for the complete oxidation. This study was to investigate the oxidation efficiency of the catalyst at different ozone ratios; therefore, the O_3/MEK ratios of 3, 7, and 11 were tested.

Results and discussion.

The concentrations of MEK, ozone, and CO_2 after the catalytic oxidation were measured in the column outlet. More than 99.9% of ozone was removed by the catalytic reaction at all the O_3/MEK ratio of 3, 7, and 11. The MEK removal rates were 23.9%, 91.3%, and 97.8%, respectively. It is interesting to note that the MEK removal rate was greater than 90% at the O_3/MEK ratio of 7, which is less than the stoichiometric ratio required for the complete oxidation. Consequently, the Mn catalyst prepared in this study showed the MEK and ozone removal rates greater than 90% at room temperature, even though the O_3/MEK ratio was less than the stoichiometric complete oxidation. However, the CO_2 conversion rates were found to be 27.7%, 59.3%, and 97.7% at the O_3/MEK ratio of 3, 7, and 11, respectively, showing that the CO_2 conversion rate decreased with decreasing the O_3/MEK ratios.

By-products generated from the catalytic ozonation of MEK were qualitatively analyzed, and 2,3-butanedione was the most abundant compound. Methyl acetate, acetaldehyde, and acetic acid were also found after the ozonation of MEK. As the O_3/MEK ratio increased, the conversion of 2,3-butanedione to fewer carbon compounds including methyl acetate, acetaldehyde, and acetic acid was prompted. Further studies on the oxidation mechanisms and catalyst poisoning by the accumulation of the by-products are required under various O_3/MEK ratios.

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Amino-Modified Ruthenium Nanoparticles as Efficient and Selective Catalysts for the Partial and Complete Reduction of Quinolines

Adhwa A. Alharbi[1], Thomas W. Chamberlain[2*], Julian G. Knight[1], Simon Doherty[1*]

[1] *Newcastle University Centre for Catalysis (NUCAT), School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU*

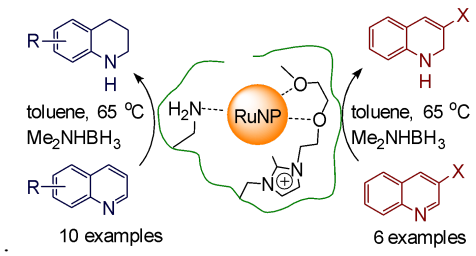
[2]*Institute of Process Research & Development School of Chemistry and School of Chemical and Process Engineering, University of Leeds, Woodhouse Lane, LS2 9JT, UK*

[*] *Corresponding Authors. E-mail Addresses: simon.doherty@ncl.ac.uk (S. Doherty), t.w.chamberlain@leeds.ac.uk (T. W. Chamberlain)*

Abstract:

RuNPs stabilised by an amino-decorated imidazolium-based polymer immobilized ionic liquid is a remarkably efficient catalyst for the dimethylamine borane mediated reduction of quinolines to 1,2,3,4-tetrahydroquinoline (THQ) via 1,2-dihydroquinoline (DHQ). The initial TOF of 610 mol of quinoline converted mol Ru^{-1} h^{-1} for the reduction of quinoline is among the highest to be reported for a metal nanoparticle-based catalyst. Under optimised conditions, a wide range of substituted quinolines were reduced to a mixture of the corresponding 1,2-dihydroquinoline and 1,2,3,4-tetrahydroquinoline in short reaction times and ultimately to the 1,2,3,4-tetrahydroquinoline as the major product by extending the reaction time accordingly. Remarkably, the reduction of 3-substituted quinolines occurred with 100% selectivity for the corresponding partially reduced 1,2-dihydroquinoline, which wwas obtained as the sole product in near quantitative yield. Hot filtration experiments showed that the active species was heterogeneous and post reaction analysis of the catalyst using TEM revealed that the nanoparticles remained monodisperse with an average diameter of 1.8 nm which is similar to that of a freshly prepared sample of catalyst.

Graphical Abstract



Kinetic Modeling Based on Complex Reaction Theory for Catalytic Deep Desulfurization over Modified UiO-66 Metal Organic Framework

Bijan Barghi[1*], Tanel Mõistlik[1*], Oliver Järvik[2], Allan Niidu[1]

[1] *Tallinn University of Technology, Virumaa College, Kohtla-Järve, Estonia*
[2] *Tallinn University of Technology, School of Engineering, Tallinn, Estonia*
[*] *bijan.barghi@taltech.ee*

Keywords: Oxidation, Metal Organic Framework, Modified UiO-66, Kinetic Modeling, Complex Reaction

Introduction. As improving deep desulfurization is essential for producing ultra-clean sulfur-free fuel, Catalytic Oxidation Desulfurization (CODS) is a practical approach for removing planar sulfur compounds.[1] CODS process includes oxidation and the extraction step for the removal. The porous zirconium terephthalate UiO-66 provides a significant contribution to catalytic purposes because of its large surface area, tunable porosity, and reusability.[2] The insertion of functional groups into organic linkers affect on the ODS performance of UiO-66(Zr) due to electron induction effect.[3] Introduction of nitro-group in BDC linker can reduce the electron density of Zr sites in UiO-66 via the benzene ring conduction and thus enhance the ability to gain electrons and therefore increasing the Lewis acidic nature of zirconium clusters. Ultimately leading to stronger interaction with aromatic sulfur containing compounds. UiO-66-NO_2 exhibited superior catalytic activity in CODS reactions because it has a strong ability to gain electrons.[3] In this study, a systematic procedure[4] is applied to derive the overall rate equation expressions for reactant/product molecules cooperated in the reaction networks based on the theory of complex reactions for DBT removal in CODS reaction over UiO-66-NO_2.

Experimental/methodology. Heterogeneous catalytic oxidation is a multi-component reaction procedure that goes through elementary reaction steps. The mathematical procedure of the overall reaction has been employed by MATLAB to justify the overall items of complex kinetic mechanisms. The approach of overall reaction has been applied for this study to investigate the mechanism of CODS of Dibenzothiophehe (DBT) over MOF. The proposed combined mechanism consists of 11 elementary reaction steps. CODS reactions were conducted in a 22 mL reactor. For the model fuel (MF), 1000 ppm of DBT was dissolved in n-dodecane, and with the volume ratio 1:1, acetonitrile was added to the reactor as the polar phase. According to the experiment design, the specified amount of MOF was added to the reactor; then, hydrogen peroxide was supplied after heating the reactor to a predefined temperature. The aqueous and fuel phase was collected after the reaction had been completed and then analyzed.

Results and discussion. Predicted values of component yield including DBT, its sulfone and, sulfoxide were in appropriate accordance with the experimental data. Eventually, this study smooths the way for similar research toward the joint of complex reactions and multiple reaction/component mechanisms.



Figure 1. Procedure employed to derive the overall rate equation expressions for CODS network

Table 1. Obtained reaction routes (RR) and overall reactions for CODS over UiO-66-NO_2

Reaction Route	Expression	Overal Reaction	
RR1	S1-S3+S10	$DBT + H_2O_2 == Sulfoxide + H_2O$	N(1)
RR2	S9-S5+S10	$Sulfoxide + H_2O_2 == Sulfone + H_2O$	N(2)
RR3	S4-S9+S10-S6	$RS + Sulfone == 2Sulfoxide$	N(3)
RR4	S3-S5+S7-S8	-	N(4)
RR5	S2+S4+S10	$DBT + H_2O_2 == Sulfoxide + H_2O$	N(5)
RR6	S11+S7-S5+S2	-	N(6)

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First Principles Investigation of Interwoven Electronical and Energetical Properties of Pt_1O_x/CeO_2 Single Atom Catalysts towards CO oxidation

Sarah Bernart[1], Jelena Jelic[1], Felix Studt[1,2]

[1]*Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*
[2]*Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany*
[*]*felix.studt@kit.edu*

Introduction . In this study we focus on Pt single sites supported on the ceria surface facets {100}, {110} and {111} and the accordingly activity towards CO oxidation related to the environmental conditions by means of temperature and oxygen pressure. The catalyst is investigated by DFT methods on a GGA+U level of theory and the Bader analysis. The Mars-van Krevelen and the Langmuir-Hinshelwood mechanism were studied to describe the surface oxygen chemistry of the ceria supported noble metal. The temperature dependence between the competing rate-limiting steps characteristic for each of the mechanisms were found to result in a change of the rate-limiting barriers heights by increasing temperature.

Methodology. The DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) [1,2] in connection with the Atomic Simulation Environment (ASE) [3]. A plane-wave basis set with a cut-off energy of 415 eV [4], the projector augmented wave method [5, 6] and the Bayesian error estimation functional with van der Waals (BEEF-vdW) [7] exchange correlation functional were used. Due to the localized Ce 4f orbitals in ceria, we applied the generalized gradient approximation (GGA) + U (U = 4.5 eV for the 4f electron of ceria in the implementation of Cococcioni and de Gironcoli. [8, 9]

Results and discussion. The Langmuir-Hinshelwood mechanism investigated in this study involves no surface lattice oxygen vacancy. The first step is a dissociation of a O_2 molecule adsorbed directly on the Pt single site leading to a $Pt^{+IV}O_2$ species. The Mars-van Krevelen mechanism investigated in this study involves one surface lattice oxygen vacancy.

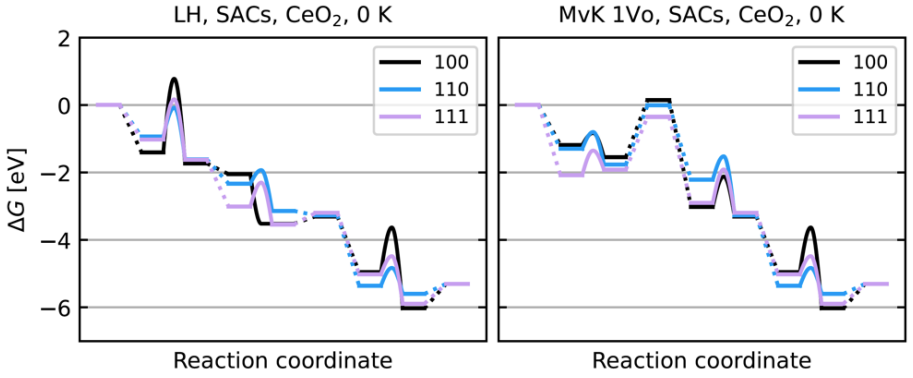

Figure 1: Potential energy diagrams of the Langmuir-Hinshelwood and the Mars-van Krevelen mechanism for the CO oxidation on the ceria surface facets {100},{110} and {111}.

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Magnetism in catalysis: Pt_3M (111) (M=Fe, Co and Ni) as case study

C. Biz[1,2]*, M. Fianchini[1], J. Gracia[1]*

[1]*MagnetoCat SL, General Polavieja 9 3Izq (03012), Alicante, Spain*
[2]*Universitat Jaume I, Av. Vicente Sos Baynat s/n, E-12071 Castellón de la Plana, Spain*
[*]*chiara.biz@magnetocat.com, jose.gracia@magnetocat.com*

Keywords: heterogeneous catalysis, ORR, magnetism, DFT+U, segregation

Introduction. In the last years the relationship between magnetism and heterogeneous catalysis has regained substantial attention since the pioneering works of Selwood[1] and Hedvall[2] in mid-20th century. An outstanding example of this relationship is represented by Pt-bimetallic alloys containing ferromagnetic metals like Fe, Co and Ni, which have been experimentally investigated as good candidates for cathode materials in Proton Exchange Membrane fuel cells[3]. Since the electronic structure-atomic structure-catalytic activity correlation is at the root of catalysis, the possibility of the influence of magnetic properties in the catalytic activity of these compositions cannot be neglected. Here we present a computational study on the influence of magnetism in the structural, chemisorption and stability properties of multilayered Pt_3M (M= Fe, Co, Ni) (111) compositions.

Experimental/methodology. The work is performed by PBEsol + U method (U= 2.4 eV)[4,5]. Spin- and non-spin calculations are carried out to understand the influence of spin potentials in the atomic arrangement, chemisorption and resistance against segregation of Pt_3M (M=Fe, Co, Ni) (111) alloys[4,5].

Results and discussion. The study begins with a detailed structural screening of Pt_3M (M= Fe, Co, Ni) slab models with different atomic distributions. The global minima for all the three compositions are found to be ordered structures with multilayer organization among the magnetic 3*d*-metals and the non-magnetic metal Pt (see Figure 1)[4,5]. The chemisorption enthalpy values of O* atoms on these magnetic (FM and AFM A-type) multilayered models show a weaker binding of about 0.16-0.22 eV in comparison with the non-magnetic isostructural ones[4]. Moreover, magnetic multilayered $Pt_3Fe(111)$, $Pt_3Co(111)$ and $Pt_3Ni(111)$ also show a general good resistance against the segregation of FM 3*d*-metal atoms under vacuum and oxygen environment[4]. In the case of the non-magnetic isostructural slabs such stability is preserved under vacuum only, while the lack of magnetic interactions favours the segregation of 3*d*-metals when oxygen atoms are chemisorbed onto their surfaces[4]. These results show that a complete and realistic treatment of the electronic structure-atomic structure−activity relationships in heterogeneous catalysis relies on the correct evaluation of orbital magnetism.

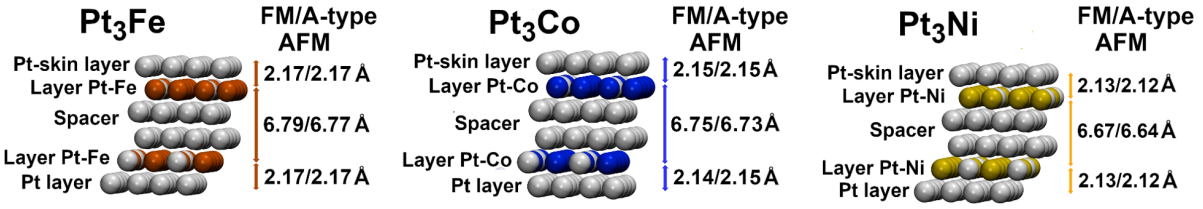

Figure 1. Multilayered organization of the global minima $Pt_3Fe(111)$, $Pt_3Co(111)$, and $Pt_3Ni(111)$ nanostructures with estimated distances (in Å) between the layers for the FM (right) and A-type AFM (left) orderings, respectively.

Acknowledgments

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Interpretation of transient effects on NH_3 oxidation over Pt/Al_2O_3: an experimental and modelling study for automotive applications

R. Bono*[1,2], R. Uglietti[2], G. Keitl[2], A. Scheuer[2], A. Dreizler[1], M. Votsmeier[1,2]

[1]*Reaktive Strömungen und Messtechnik, Technische Universität Darmstadt, Darmstadt, Germany*
[2]*Umicore AG & Co. KG, Hanau, Germany*
**bono@rsm.tu-darmstadt.de*

Introduction. To decrease tail-pipe emissions of NH_3, the implementation of the Ammonia Slip Catalyst (ASC) in the vehicles after-treatment systems has become of primary relevance. The ASC consists in a Pt/Al_2O_3 bottom layer responsible for NH_3 direct oxidation, and a top layer responsible for the Selective Catalytic Reduction (SCR) of the NO_x formed in the bottom layer. Focusing on the bottom layer, although extensive research on the mechanisms has been carried out, some significant open questions remain. In particular, the activity of the bottom layer at low temperatures (< 300 °C) has been proven to depend on the catalyst history [1], but no detailed mechanistic explanation has been given. In this study, we propose an interpretation of such phenomenon, ascribing it to the oxide formation on the Pt surface, which is known to be particularly stable at low temperatures [2]. To accomplish the task, transient experiments on NH_3 oxidation have been carried out, together with modelling the catalyst activity.

Experimental/methodology. The NH_3 oxidation activity of a Pt/Al_2O_3 wash-coated monolith, at different stages of hydrothermal aging (0 to 100 h), has been tested at different temperatures (from 150 to 300 °C), using a synthetic gas test bench and an FTIR gas analyser. For each temperature, the test has been run until steady conversion was reached. Additionally, a 1D+1D monolith model has been used to fit the transient profile of NH_3 conversion by including the reactions for Pt oxide formation and depletion.

Results and discussion. Figure 1 shows the first 5 minutes of the NH_3 conversion trend against time for each investigated temperature, with respect to the fresh sample. At the beginning of the test, no oxygen is fed in the system and no oxide is present on the Pt surfaces. Then, O_2 is fed to the reactor, initiating the NH_3 oxidation. Around 30 seconds, an initial maximum is reached, which has been ascribed to the conversion on an oxide-free Pt surface. Afterwards, above 260 °C, a stable catalyst activity is observed. Instead, at lower temperatures, the catalyst shows a progressive deactivation, until a steady conversion is achieved. This effect has been ascribed to the slow formation of detrimental Pt oxides over time, hindering the conversion. Afterwards, we have applied this concept to a 1D+1D monolith model, and the simulations of both fresh and aged states are ongoing.
As a whole, this work provides new insights on the Pt bottom layer activity at low temperatures, which are of primary interest in the automotive industry.

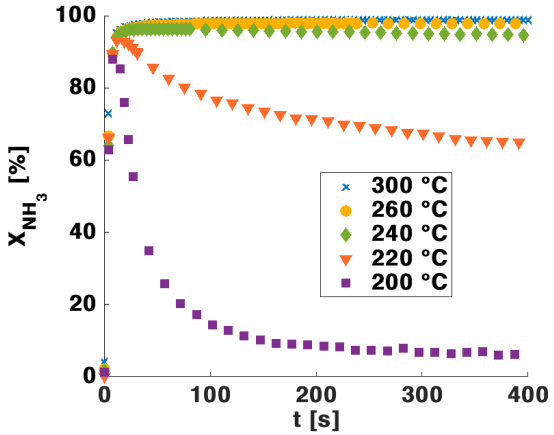

Figure 1: transient NH_3 conversion at different temperatures. NH_3 conversion hysteresis against T.

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Advancing alkaline organic electroreductions by tuning H adsorption on the cathode

Anna Ciotti,[1*] Tengfei Li,[2] Motiar Rahaman,[2] Yeung Wing See,[2] Arjun Vijeta,[2] Erwin Reisner,[2] Max García-Melchor[1]

[1] *School of Chemistry, Lloyd Institute, Trinity College Dublin, The University of Dublin, Dublin, Ireland*

[2] *Yusuf Hamied Department of Chemistry, University of Cambridge, Cambridge, UK*

[*] *ciottia@tcd.ie*

Keywords: electrochemical hydrogenations, H_2 evolution, surface coverages, catalyst design, DFT.

Introduction. Industrial hydrogenations of platform chemicals often employ organometallic catalysts and organic solvents.[1] One way to cut down the associated chemical waste is the electrification of such processes by replacing organometallic reagents with electrodes based on earth-abundant elements, and organic solvents with H_2O and alcohols.[1] However, the use of aqueous electrolytes is hindered by the competition with the hydrogen evolution reaction (HER).[2] As HER activity is reduced under alkaline conditions,[2] we propose that the ideal catalyst for electrochemical hydrogenations (ECH) should work efficiently at basic pH, hydrolysing H_2O to source the H atoms for the subsequent hydrogenation steps. H atoms should also be retained on the surface with close to thermoneutral binding strength (ΔG_{*H}) at the applied potential, and the catalyst should be based on abundant and cheap elements. With these premises, we computationally guided the design of cost-efficient metal cathodes for the ECH of acetophenone (AC) to 1-phenylethanol.

Methodology. Periodic DFT calculations with the Bayesian error estimation functional (BEEF)[4] were carried out using the Vienna Ab Initio Simulation Pacakge (VASP, version 5.4.4) [3] and an energy cut-off of 500 eV for the plane waves. The Brillouin zone was sampled with a Γ-centered 5×3×1 k-point mesh.

Results and discussion. As H_2O hydrolysis is unfavourable on AC,[5] a catalyst exhibiting a H coverage was sought to achieve this model ECH. To prove our hypothesis, we employed metal cathodes covering a wide range of ΔG_{*H}, *i.e.* Ag, Au, Cu, In, Ni and Pt. Calculations indicated that Ag(111) and Au(111) exhibited 25% of the *fcc* sites occupied by H atoms with moderately endergonic ΔG_{*H} values under relevant ECH conditions. On the other hand, Cu(111) featured 75% of such sites covered with H atoms and moderately exergonic ΔG_{*H}, while Ni(111) and Pt(111) presented all those sites terminated with H atoms and highly exergonic ΔG_{*H} (*Fig. 1a*). Finally, we predicted the In(101) surface to be clean due to the highly endergonic ΔG_{*H} (*Fig. 1a*). Based on these findings, we envisioned the best ECH activity with Ag, Au and Cu, and poor conversions with In, which lacked the H coverage, Ni, which had to pay a higher energy penalty for H desorption and AC hydrogenation, and Pt, due to its outstanding HER activity.[2] These predictions were confirmed both experimentally (*Fig. 1b*) and computationally with detailed mechanistic studies, which unveiled the role of solvent H_2O molecules which shuttle H atoms from the surface coverage to AC (*Fig. 1c*). Overall, this work demonstrates the importance of assessing the surface coverage of electrocatalysts under relevant conditions, and highlights the power of joint computational and experimental studies in guiding the discovery of materials to electrify industrial chemical syntheses.

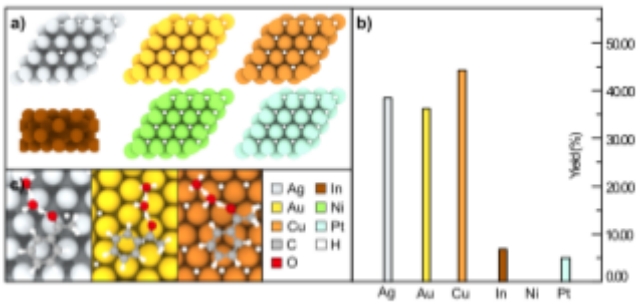

Figure 1. **a**) Electrodes resting states under ECH conditions. **b**) Yields (%) of AC-ECH. **c**) TSs of AC-ECH on Ag, Au and Cu.

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Theoretical modeling of pathways for the transformation of glucose and fructose to levulinic acid using sulfuric acid.

A. Kącka-Zych[1], N.Sobuś[1], I.Czekaj[1*]

[1] *Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Krakow, POLAND*
**izabela.czekaj@pk.edu.pl*

Keywords: sulfuric acid; glucose, fructose, DFT; Biomass; Levulinic acid

Introduction

Levulinic acid (LA) has been identified as a promising biocompound derived from biomass. It is a platform molecule that is used as a precursor for pharmaceuticals, plasticizers and various other additives (Figure 1) [1,2]. LA arises as a result of depolymerization and dehydration of the cellulose fraction [3]. Theoretical modeling involved understanding the changes that occur during the conversion of glucose to levulinic acid (LA) proceeding in the presence of an H_2SO_4 catalyst.

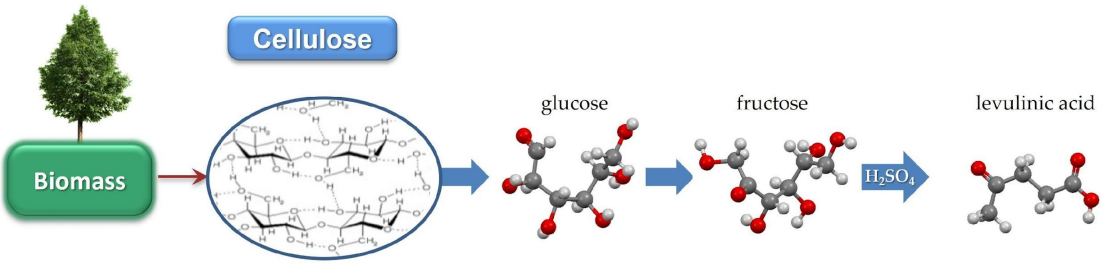

Fig. 1. Reaction pathways of biomass into glucose and levulinic acid.

Experimental/methodology.

All calculations associated to the conversion of sugars to levulinic acid were performed using: the Gaussian (PBE0 functionals, 6-31G(d,p) and 6-311+G(d,p) basis sets), the (QST2) algorithm for TSs. the conceptual density functional theory (CDFT) for global reactivity indices (GS, B3LYP/6-31G(d) level), the TopMod for Electron Localization Function (ELF).

Results and discussion.

Modeling included the conversion of glucose to fructose, fructose to hydroxymethylfurfural (HMF), and then HMF to levulinic acid without/with H_2SO_4 and in different temperatures (298 and 493K). Two mechanisms of glucose to fructose conversion were considered: cyclic and open chain mechanism. Cyclic mechanism is forbidden from kinetic point of view at low temperature. At higher temperatures both paths are allowed. Conversion of fructose via HMF to LA involves the steps of protonation/deprotonation and dehydration reactions as well as formic acid desorption.

Acknowledgments

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Reactivity of Vanadium V(II) Cationic Sites in Si-Rich Zeolites

Stepan Sklenak, Jiri Dedecek, Agnieszka Monika Kornas, Edyta Tabor

[1]*J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 3, Prague, Czech Republic*

[*]*stepan.sklenak@jh-inst.cas.cz*

Introduction.

Transition metal exchanged Si-rich zeolites are promising materials for redox-catalysis [1]. The periodic DFT methodology allows a modeling of the reactivity of transition metals exchanged in zeolites [2]. Periodic DFT calculations of the reactivity of two cooperating transition metal cations in zeolites were essential for the discovery of a new type of the active sites capable of the M(II) to M(IV) redox cycle able to activate small low reactive molecules [3,4].

Methodology.

Periodic DFT employing the VASP program.

Results and discussion.

In this contribution, we report on our study of the reactivity of vanadium V(II) cationic sites with small molecules as, for example, dioxygen. We describe the redox behavior and show that vanadium V(II) cationic sites exhibit desired redox properties for the selected catalytic reactions.

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Ketonisation of Organic Acids over ZrO_2-based catalysts for Biomass Valorisation: The Role of Surface Acid-Base Sites

M. Delarmelina[1,2*], Gunjan Deshmukh[2,3], Haresh Manyar[2,3], C. Richard A. Catlow[1,2]

[1]*School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK*
[2]*UK Catalysis Hub, Research Complex at Harwell, Oxfordshire OX11 0FA, UK*
[3]*School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, UK*
[*]*DelarmelinaM@Cardiff.ac.uk*

Keywords: Biofuels, Carboxylic acids, Ketonisation, Zirconia, DFT.

Introduction. Production of liquid fuels from biomass have gained increasing industrial and academic attention as alternative energy source to fossil-based fuels. Biofuels are usually obtained as a mixture of organic species with high content of oxygenated derivatives, which required chemical upgrading for improvement of its physicochemical properties prior to their use as fuels.[1] Acid–base bifunctional catalysts are particularly desirable in this context, which can be tuned by different approaches in order to optimise their activity and selectivity.[2] Here, we investigate how distinct dopants can affect the acid-base properties of zirconia based catalysts and their effect over the ketonisation of organic acids.

Experimental/methodology. All calculations were performed using the VASP package within the framework of periodic density functional theory and at RPBE-D3+U ($U_{Ti(d)}$ = 4.0 eV) level. The Zr $4s^2 4p^6 4d^2 5s^2$ and O $2s^2 2p^4$ orbitals were explicitly included as valence electrons. Brillouin zone sampling was performed using the Monkhorst–Pack scheme with a k-point grid of 5 × 5 × 1 together with a Gaussian smearing broadening of 0.02 eV. Forces and electronic SCF convergence were set at 10^{-2} eV $Å^{-1}$ and 10^{-5} eV, respectively. All surfaces were previously constructed and characterised regarding their acid-base properties.[2,3]

Results and discussion. The ketonisation reaction has been proposed to occur via several putative mechanisms. Currently, the β-ketoacid mechanism is the most plausible one based on previous experimental and computational results.[1] The two most important steps of the β-ketoacid mechanism are investigated here: enolisation of the adsorbed organic acid and C-C coupling step to afford α-hydroxy γ-carboxy alkoxide intermediate (**Table 1**). According to the computed energy profile, the rate-determining step for the acetic acid reaction over clean c-ZrO_2 (111) is the enolisation step ($E_{barrier}$ = 36.1 kcal mol^{-1}). Similar results were computed for propionic acid. The computed energy barrier for the C-C homo- and cross-coupling step presented only slight variations, ranging between 16.7 and 20.3 kcal mol^{-1}.

Table 1. Energy profile for enolate formation and C-C coupling of acetic acid over c-ZrO_2 (111). Reactivity of acetic acid is compared for selected examples of modified zirconia surfaces. Energies are given in kcal mol^{-1}.

Acetic acid	HAc_{ads}	TS_{enol}	Enolate	2nd HAc_{ads}	TS_{C-C}	Interm.
c-ZrO_2 (111)	-38.4	-2.3 (36.1)	-22.3	-43.1	-26.4 (16.7)	-38.9
t-ZrO_2 (101)	-43.9	-16.2 (27.7)	-33.4	-67.9	-46.6 (21.3)	64.6
Ca-doped c-ZrO_2 (111)	-53.2	-30.6 (22.6)	-37.1	-74.8	-35.5 (39.3)	-59.0
Y-doped c-ZrO_2 (111)	-52.4	-29.4 (23.0)	-38.4	-72.6	-51.1 (21.5)	-60.3

Two examples of modified surfaces investigated here are also shown in **Table 1**: Ca- and Y-doped c-ZrO_2 (111). Interestingly, a significant drop in the energy barrier for enolisation was computed for both doped surfaces. On the other hand, the computed barriers for the C-C coupling step were distinctly modified for these same systems: reduction over Y-doped c-ZrO_2 (111) and increase over Ca-doped c-ZrO_2 (111). The origin of such effect is shown to be due to distinct strength of acid-base pairs and adsorption modes, as well as resulting changes to TS structures. These findings are used in the rationalisation of the role of distinct dopants over the ketonisation reaction of organic acids. Furthermore, they provide insight into the identification of more eficient and selective catalysts for the chemical upgrading of biofuels.

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A Revised Paring Mechanism for the MTO-process in Acidic Zeolites

A. E. Enss[1*], P. Huber[1], P. N. Plessow[1], F. Studt[1,2]

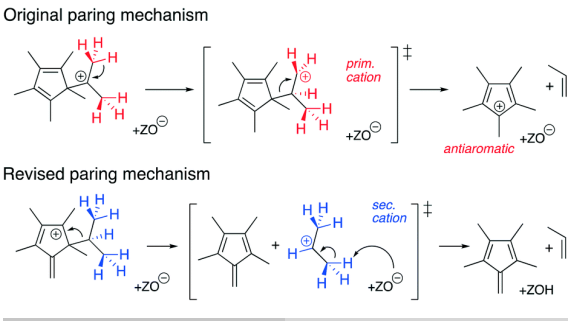
[1]*Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany*
[2]*Institute for Technical Chemistry and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany*
[*]*annika.enss@kit.edu*

Keywords: MTO-process, aromatic cycle, paring mechanism, DFT calculations

Introduction. The methanol-to-olefins process is a possible way to convert sustainably produced methanol into valuable chemicals, without relying on fossile resources. It is catalyzed by acidic zeolites such as H-ZSM-5 or H-SAPO-34 [1]. The mechanism constists of two competing cycles using either olefins or aromatic species as co-catalysts. The aromatic cycle also consists of two possible sub-cycles, namely the paring and the side-chain mechanism [2]. The paring mechanism was in previous literature considered to be unfavorable because of its antiaromatic intermediate and therefore high reaction barrier [2]. Recently, we presented a new possible paring mechanism with significantly lower reaction barriers on the H-SSZ-13 model catalyst [3]. In this work, we employ this revised paring mechanism to the industrially relevant H-SAPO-34 and H-ZSM-5 zeolites.

Methodology. H-ZSM-5 and H-SAPO-34 were used as model catalysts. Periodic DFT calculations were carried out with the Vienna Ab Initio Simulation Package (VASP) version 5.4.1 in the atomic simulation environment (ASE) using the PBE-D3 functional and the projector-augmented wave method. Transition state searches were performed with automated relaxed potential energy surface scans (ARPESS) [4]. Energy corrections at the CCSD(T)-level of theory were employed by single-point calculations on smaller clustermodels of the active site, as described previously [5].

Results and discussion. In both investigated zeolites, a similar paring mechanism as described in [3] was observed. The crucial step that distinguishes the newly proposed mechanism from the mechanism described in the literature is the propene elimination step, which occurs in our mechanism from a neutral isopropyl fragment, involving also protonation of the zeolite's acid site, as shown in fig. 1. This step was found to be comparable for both H-SAPO-34 and H-ZSM-5, with barriers being lower than the respective H-SSZ-13 barrier (< 142 kJ/mol). This indicates, that the proposed new paring mechanism is more feasible also in industrially employed catalysts.



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Relating WGS Performance to Oxygen Storage Capacity (OSC) under Realistic Feed

B. M. Eropak[1,2], G. Öztürk[1], B. Selen Çağlayan[2,3], A. E. Aksoylu[1,2*]

[1]*Department of Chemical Engineering, Boğaziçi University, Bebek, Istanbul 34342, Turkey*
[2]*SNG&HydTec Lab, Science and Technology Building, Boğaziçi University, Kandilli, Istanbul 34684, Turkey*
[3]*Advanced Technologies R&D Center, Boğaziçi University, Bebek, Istanbul 34342, Turkey*
[*]*aksoylu@boun.edu.tr*

Keywords: WGS performance, oxygen storage capacity, OSC and performance relation

Introduction. There has been a profound research interest in the design and development of active, steam tolerant, non-pyrophoric, robust Platinum-group metal (PGM) based and metal oxide supported WGS catalysts to be used in a fuel processor (FP) producing PEM grade hydrogen for PEM fuel cells. The current work mainly focuses on developing a reliable methodology for determination of oxygen storage capacity (OSC) of the catalysts through the use of operando IGA-MS analysis and establishing a relation between WGS activity and OSC.

Experimental. Pt-Re-V/CeO_2 catalysts were prepared, characterized and tested in WGS performance tests for two realistic feed compositions, which have H_2O/CO ratio 6.7 and 16.2, at 300, 350, 400 and 450°C for fixed GHSV at 120,000 ml $gcat^{-1}$ h^{-1}. The OSC values of the samples were determined through a novel operando IGA-MS methodology under two diluted realistic feed (DRF) compositions at 350°C. Experiments conducted with pure He flow over each catalyst at all temperature levels were used to determine the "structural" oxygen that already exist in the catalysts/their structure (S-OSC). However, the experiments conducted upon DRFs display not only the oxygen stored in lattice and located on surface in the form of surface groups as formate, carbonate and/or carboxyl-carboxylate like intermediates, but also the oxygen emanating from reaction; which in all can be called as "total" OSC (T-OSC). Effective OSC (E-OSC) was obtained as the difference between T-OSC and S-OSC for a specific reaction temperature.

Results and discussion. The catalysts showed their highest performances at 350 and 400 °C and the highest net H_2 production values were achieved over 1Pt-1Re-1V and 0.5Pt-0.5Re-0.5V catalysts at 350 and 400 °C, respectively under feed flow having low H_2O/CO ratio. Figure 1 represents three types of OSC values obtained for each catalyst subjected to diluted realistic feed flows, which have H_2O/CO ratio 6.7 and 16.2 at 350°C. The combined evaluation of WGS performance and OSC results indicates that S-OSC including surface groups have key role in water activation at the time when reactive mixture first contacts with the catalyst, while E-OSC becomes primary factor affecting WGS activity after the surface concentrations reach steady state.

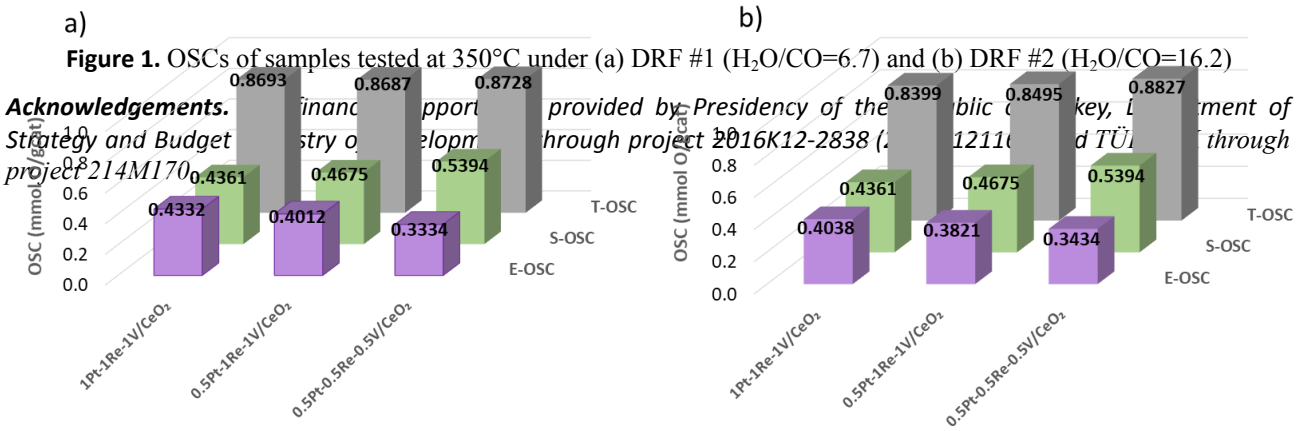

Figure 1. OSCs of samples tested at 350°C under (a) DRF #1 (H_2O/CO=6.7) and (b) DRF #2 (H_2O/CO=16.2)

Acknowledgements. *[illegible] financ[illegible] pport[illegible] provided by Presidency of the [illegible]blic [illegible]key, [illegible]ment of Strategy and Budget [illegible]stry o[illegible]elopm[illegible] through project 2016K12-2838 ([illegible]1211[illegible]d TÜ[illegible] through project 214M170.*

Ethane dehydrogenation in the presence of CO_2 over Co/BEA catalyst: effect of cobalt precursors and catalytic performances

Safaa ESSID*,Roman Bulánek

University of Pardubice, Faculty of Chemical Technology, Department of Physical Chemistry, Studentská 573, CZ53210 Pardubice, Czech Republic
*safaa.essid@upce.cz

Keywords: ethane, CO_2, ethene, cobalt, BEA

Introduction. The conversion of ethane into ethene with economically significant activity and stability is an advance from an industrial point of view and would add value to ethane a reliable source of more valuable chemical products. Ethylene is one of the most important and adjustable intermediates for synthesis of various chemical industry. Another big challenge of the chemical industry is utilization of CO_2, which considered as the main cause of global warming. Accordingly, the tandem CO_2-assisted dehydrogenation of ethane to ethylene is a potential way, since the reaction equilibrium can be shifted as a result of H_2 consumption via reverse water-gas shift reaction ($H_2 + CO_2 \rightarrow H_2O + CO$), and contribute to decrease the rate of coke formation reaction ($C + CO_2 \rightarrow 2CO$)[1].

Experimental/methodology. Giving the fact that, Co-zeolites performances in CO_2 ethane dehydrogenation were poorly investigated in the literature [1] [2], our goal was to contribute to enrich the discussion and to understand the role of cobalt oxidation states in the CO_2-ethane dehydrogenation into ethene.

Here, a series of Co/BEA catalysts were prepared by solid state ion exchange using differents cobalt precursors (cobalt chloride, cobalt nitrate, cobalt acetate and cobalt acetylacetonate) exchanged with BEA zeolite (Si/Al=12.5). Worthily, a deep chracterization was performed using temperature programmed reduction, FT-IR and DR UV-vis spectroscopy in order to shed light into the distribution of cobalt species on the zeolite surface and in the cationic sites.The prepared catalysts were tested in CO_2-ethane dehydrogenation performed at 575 ◦C in a fixed-bed through flow microreactor at atmospheric pressure. 200 mg catalyst (35~60 mesh) was activated in situ under He flow at 575◦C for 2 h before dehydrogenation. The gaseous reactant contained (3% ethane, 6% CO_2 with the balance helium) at a total flow rate of 30 mL/min. The products were analyzed using an on-line gas chromatograph (GC) equipped with flame ionization detector (FID) and a thermal conductivity detector (TCD) .

Results and discussion. Various cobalt species were formed in zeolites materials, including isolated cationic Co^{2+}, CoO_x clusters , $[Co(III)O]^+$ and Co_3O_4 particles depending on the cobalt precursors used. In fact, the cobalt distribution in the zeolite surface was highly affected by variyng the cobalt precursors. Mainly, in the case of Co/BEA prepared with cobalt chloride, we noticed the relatively high occupation of cobalt Co^{2+} in the zeolite cationic sites and cobalt oxo-species $[Co(III)O]^+$, revealed by UV-Vis spectroscopy. This catalyst was the most active one in this work exhibiting an ethane conversion of 15% with around 82% selectivity toward ethene at 575◦C. In the case of Co/BEA catalyst prepared with cobalt nitrate, where TPR and UV-vis spectroscopy revealed that cobalt was present mainly in the form of CoO_x clusters, was observed negligible activity in the CO_2- ethane dehydrogenation, but high activity in the CO_2 reduction to CO. Although, cobalt acetate and cobalt acetylacetonate, showed the presence of Co_3O_4 and CoO_x reduced at lower temperature when compared to TPR results of Co/BEA catalyst prepared with cobalt chloride, these catalyst where selective to ethene as main product. In brief, it should be pointed out, that cobalt in the oxides forms (Co_3O_4 and CoO_x) with particular sizes could be reduced in situ to Co(II) during the CO_2-ethane dehydrogenation and lead to high activity and selectivity into the desired product.

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2

Cu-based double metal cyanides for phosphoramidate synthesis via aerobic oxidative coupling of amines and phosphites

Alejandro Fonseca, Kwinten Janssens, Carlos Marquez*, Dirk De Vos*
cMACS, Celestijnenlaan 200F, 3001 Leuven, Belgium.
* carlos.marquez@kuleuven.be, dirk.devos@kuleuven.be

Keywords: Double Metal Cyanides, Heterogeneous catalysis, Green Chemistry, Phosphoramidates

Introduction. Phosphoramidates are common and widespread backbones of a great variety of fine chemicals, pharmaceuticals, additives and natural products.[1,2] Conventional approaches to their synthesis make use of toxic chlorinated reagents and intermediates, which are sought to be avoided at an industrial scale.[3] A more environmentally friendly approach to the phosphoramidate synthesis is the metal-catalyzed aerobic oxidative coupling of phosphites and amines, with homogeneous Cu salts showing promising results.[4] Here we report the first heterogeneously catalyzed aerobic oxidative coupling of phosphites and amines promoted by a $Cu_3[Co(CN)_6]_2$-based double metal cyanide (Cu-Co DMC), using I_2 as additive and O_2 as reactant. This represents an efficient, environmentally friendly alternative to the synthesis of these valuable compounds.

Experimental/methodology. Cu-Co DMCs were prepared following previously reported procedures.[5] Reactions were performed in a sealed glass vial with magnetic agitation containing Cu-Co DMC (3 mol%), 2 ml of solvent, the corresponding phosphite (2 mmol), 2 ml of a 15 mol% I_2 solution and 4 mmol of the respective amine (4 mmol), connected to an O_2 filled balloon, bubbling into the reaction medium through a syringe. The reaction products were analysed using GC-FID, GC-MS and NMR.

Results and discussion. Preliminary experiments proved that catalytic amounts of I_2 could greatly improve the outcome of the transformation, in combination with bubbling of O_2 into solution. When the Cu-Co DMC was tested, yields up to 99% were obtained for the coupling of 2phenylethylamine and dibutyl phosphite under optimal conditons, outperforming other heterogeneous (CuO, Cu/SiO_2, Cu-BTC and Cu-Mg Al mixed oxides) and homogenous Cu catalysts ($Cu(OAc)_2$ and CuI). Interestingly, characterization by PXRD, FTIR and XAS confirmed a change in the internal crystalline structure of the DMC and the formation of different phases during its reuse, with Cu adopting an octahedral, tetrahedral and square planar coordination (Fig. 1). However, the observed changes did not have an impact on the remarkable activity of the catalyst, which could also be used for 5 iterations without any loss of activity. The scope of the reaction was also extended to the synthesis of different phosphoramidates using bulkier primary amines, secondary amines and even amides. Preliminary mechanism studies suggest that the reaction proceeds by a change in the oxidation state of the Cu metal, induced by a O_2/I^- redox cycle.

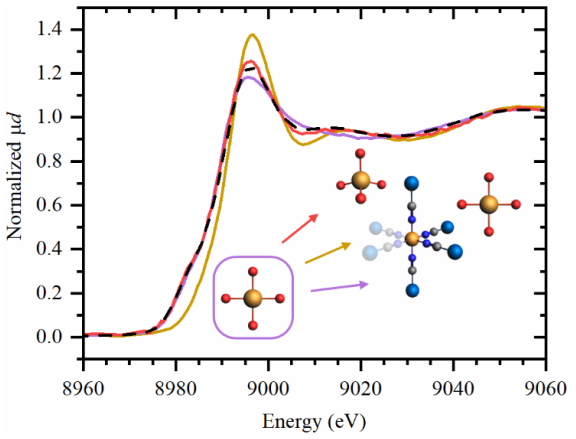

Fig. 1. Experimental Cu K-edge XANES spectra for initial (dark yellow), spent (purple) and washed (red) catalyst. The dashed line corresponds to the linear combination fit of the spectrum of the washed state using three experimental spectra (initial, spent, and tetrahedral Cu_2O)

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Mechanistic DFT study of isobutanol to butenes transformations catalyzed by acidic zeolites

M. Gešvandtnerová[1*], T. Bučko[1,2], P. Raybaud[3], C. Chizallet[3]

[1]*Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská Dolina, SK-84236 Bratislava, Slovakia*

[2]*Institute of Inorganic Chemistry, Slovak Academy of sciences, Dúbravská Cesta 9, SK-84236 Bratislava, Slovakia*

[3]*IFP Energies nouvelles Rond-Point de l'échangeur de Solaize, BP3, 69360 Solaize, France*

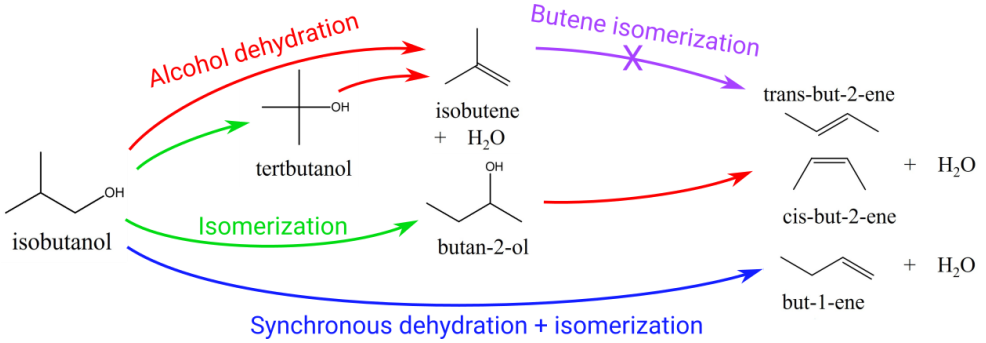
[*]*gesvandtnerova2@uniba.sk*

Keywords: heterogeneous catalysis, DFT, free energy of activation, energy span concept, catalytic cycles

Introduction: Valorization of biomass and other renewable resources is one of the major research directions in green chemistry. Dehydration of butanols to butenes catalyzed by acidic zeolites is a key step for production of longer hydrocarbon chains that can be used in further industrial processing. In experimental studies[1,2] a unexpectedly high selectivity for conversion of isobutanol to linear butenes has been demonstrated, and these results motivate our computational study. In this work, we have performed simulations of the monomolecular dehydration mechanisms that are likely at the core of the high linear butene selectivity, starting from isobutanol.

Methodology: Periodic DFT calculations were performed using the VASP code with PBE functional and D2 correction to dispersion interactions. The energy span concept, specifically designed to describe catalytic cycles[3], was used to analyze the importance of the particular transformation routes that were obtained. The critical steps were explored by *ab initio* molecular dynamics with the Blue Moon Ensemble method with a sophisticated description of reaction coordinate.

Results and discussion: In addition to conventional dehydration mechanisms, we have revealed a network of monomolecular reaction transformations of isobutanol to butenes transformations involving also isobutanol isomerizations to other butanols, and synchronous isomerization and dehydration reaction mechanisms [4]. The reaction pathway in which isobutanol is converted directly into linear butene has previously never been reported in the literature. While the static approach, based on crudest statistical mechanics approximation is useful for qualitative analysis, its accuracy is often insufficient for realistic predictions[5]. This problem is resolved by explicit sampling of configuration space via *ab initio* molecular dynamics for the some of the most important pathways identified by the energy span concept. With the aid of *ab initio* molecular dynamics, free energies of activation and ultimately also the rate constants, are determined using the transition state theory. Our results suggest that the so far overlooked isobutanol isomerizations might be of a key importance for explaining the isobutanol to linear butenes selectivity. The *a posteriori* butene isomerizations, on the other hand, are shown to be rather unlikely under the relevant experimental conditions.



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Hydrogenation of Acetone to Isopropanol over Fixed-Bed Raney-Type Nickel Catalyst

Y. Gherib, P. Kukula, J. Padevět*

Ranido, s.r.o., Thákurova 531/4, 160 00 Prague, Czech Republic
** jaroslav.padevet@ranido.cz*

Keywords: Hydrogenation, Raney-type nickel, Fixed-bed

Introduction. The catalytic hydrogenation of acetone is an important catalytic process to produce highly demanded isopropanol used for fine chemical synthesis [1, 2]. The utilization of acetone produced from CO_2 and green hydrogen from solar energy and water can then provide an access to renewable isopropanol and other downstream products [3]. **Experimental.** An experimental study on acetone hydrogenation was performed by using Raney-type nickel alloy as a catalyst. Catalytic hydrogenation experiments were carried out in a fixed bed continuous flow reactor [4] and reaction parameters such as space velocity, temperature and pressure were investigated.

Results. It was found that Raney-type nickel catalyst efficiently converted acetone (>99%) to isopropanol with excellent selectivity. No traces of by-products were detected. Further studies towards improving the efficiency of the process were performed with an emphasis on the scalability to deliver a larger amount of product.

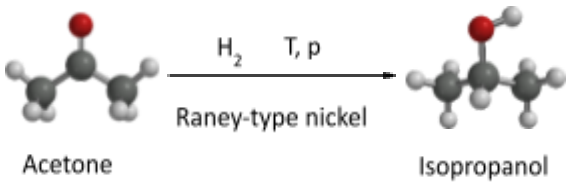

Fig. 1: Product and parameters for hydrogenation of acetone

Acknowledgements
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Quantum chemical calculations of $Pt_nD_{2n}^-$ clusters

Siddhi Gojare[1], Dennis Bumüller[1], Manuel Kraft[1], Detlef Schooss[1], Karin Fink[1]

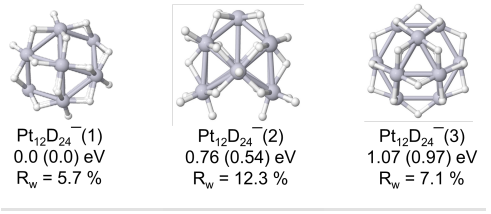
[1]*Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), 76344, Germany*

Keywords: Pt hydrides clusters, structure, spin-orbit coupling, density functional theory.

Introduction. The Pt-based heterogeneous catalysts have quite versatile catalytic properties and are applied in automotive catalytic convertors, in the catalytic oxidation and reduction reactions, and for emission control [1]. The nanoclusters of Pt show high catalytic activity and thorough study of the structure of Pt clusters in the gas phase is base in order to understand the underlying mechanisms of the surface reactions. One of the important reactions is the reaction with hydrogen. Therefore, we aim to investigate the structures of Pt-hydride cluster anions by combining trapped ion electron diffraction (TIED) techniques with DFT computations. In general, such clusters show high diversity in structures in a small energy range. This makes the task difficult to predict the global minimum structure. Heavy elements such as Pt, require to take into account the SOC which influences the relative energetic ordering of the isomers [2]. Therefore, we investigated the effect of SOC on $Pt_nD_{2n}^-$ clusters.

Experimental/methodology. The $Pt_nD_{2n}^-$ clusters were generated in the TIED experiment described in detail in ref. [3]. The scattering intensity obtained in the TIED experiment was compared with the scattering function calculated using several structure models. The structural models were obtained using combination of different methods such as semiempirical potentials within a modified genetic algorithm [4]. The best fitting structures were further optimized performing DFT calculations with the program package TURBOMOLE [5] using TPSS/def2-TZVP basis set. SOC contributions were included by relativistic two-component (2C) calculations with TPSS/dhf-TZVP-2c basis set [6].

Results and discussion. The structures and the relative energies of several isomers of $Pt_{12}D_{24}^-$ and $Pt_{13}D_{26}^-$ were investigated and were compared with the experimental data by the profile factor (R_w). The spin-orbit coupling plays a critical role in regulating the relative stability between the structural isomers of the cluster. In the case of $Pt_{12}D_{24}^-$ isomers (Figure 1), the SOC decreases the differences in the relative energies of the isomers compared to the one-component calculations. In contrast to the bare Pt_n^- clusters, inclusion of SOC did not affect the energetic ordering of the isomers. The structural motifs did not change after geometry optimization with inclusion of SOC, only a slight elongation of the Pt-Pt bond lengths was observed. Thus, it can be deduced that hydrogens stabilize the structure of Pt cluster. With the help of Nudged elastic band (NEB) method, we calculated the barrier of 1.23 eV for the transformation between isomer (1) and (2) of $Pt_{12}D_{24}^-$. In future, we want to investigate other cluster sizes, reaction with O_2, and the role of the support in catalysis.



Acknowledgments

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Development of HTC-supported non-noble metal catalysts for ammonia reforming

M. Guci[1*], F. Rümmele[1], F. Nestler[1], M. Poschmann[2], R. Szolak[1]

[1]*Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany*
[2]*Max-Planck Institute for Chemical Energy Conversion, Mülheim, Germany*
*miranda.guci@ise.fraunhofer.de

Keywords: non-noble metals, nitrogen-doped carbon, ammonia reforming, hydrogen storage/transportation

Hydrogen (H_2) is a key molecule to enable a carbon dioxide (CO_2)-neutral energy infrastructure. While the production of H_2 via renewable energy-driven water electrolysis has already achieved a high TRL, its transportation and storage remain key challenges for the implementation of the hydrogen economy [1]. Due to its beneficial storage properties, a high volumetric and gravimetric energy density and the already existing transport infrastructure, ammonia (NH_3) is a promising candidate as a H_2 carrier molecule [2]. Whereas NH_3 synthesis is today among of the best known chemical processes, the reverse, H_2 releasing reaction, i.e. NH_3 reforming, requires an energy and cost efficient thermochemical process. In particular, development of an active, stable, sustainable and cheap catalyst is needed to enable large scale H_2 production from NH_3 [3].
In the research project AmmoRef (03HY203A), Fraunhofer ISE investigates together with other academic and industrial partners the viability of nickel-, iron-, and cobalt-based catalysts for NH_3 reforming, employing an environmentally friendly biomass-derived Nitrogen-Doped Carbon (NDC) support. Besides their sutainability, NDC materials have proven their beneficial material tuning capabilities defined by selection of precursor materials, applied hydrothermal methods, doping agents, impregnation methods and post thermal treatments [4].
This contribution tends to outline the impact of metal-support interactions on the catalyst performance. Several characterization techniques, including XPS (X-ray Photoelectron Spectroscopy), XRD (X-ray Diffraction), physi- and chemisorption measurements, SEM (Scanning Electron Microscopy), were applied to understand the catalyst's structural and chemical properties with the perspective to optimize those for NH_3 reforming reaction. Experimental results revealed the highest activity for iron (Fe). Moreover, it will be shown, how the interplay of the Nitrogen (N)- precursor, post thermal treatment conditions and N-amount impact both the surface area and the activity of a Fe-based of the catalyst. Further, the influence of adding Cobalt (Co) as a second metal or promoters as Potassium or Cesium to the catalytic system will be indicated. A decline in activity for the Fe-based system was observed as the carbonization temperature of the support was raised to 800 °C. However, this trend was less when the same temperature increase was applied to a bimetallic (Fe-Co) catalytic system. This led us to the assumption that a higher graphitization degree is more beneficial for Co than Fe.
Furthermore, investigations focused on evaluating the potential of synthesizing NDC materials and its variations for coating methods are shown, aiming to assess their suitability for future industrialization.

Acknowledgments
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The role of surface silanols in the initiation of olefin metathesis on MoO_x/SiO_2 and WO_x/SiO_2 catalysts: a computational perspective

J. Handzlik*, M. Gierada, K. Kurleto

Faculty of Chemical Engineering and Technology, Cracow University of Technology, Kraków, Poland
**jhandz@pk.edu.pl*

Keywords: alkene metathesis, molybdenum, tungsten, silica, active site, mechanism, DFT.

Introduction. Metathesis of light olefins enables for regulation of olefin stocks in petrochemical industry [1]. Large-scale processes involving olefin metathesis are carried out over tungsten or molybdenum oxides supported on high-surface-area materials [1,2]. In these systems, metal alkylidene sites, being active in olefin metathesis, are formed *in situ* from the surface metal oxide species upon contact with olefin [2-5]. However, the mechanism of the transformation of the metal oxide precursors into the active sites is not well recognised, although several routes were proposed [2-5]. In this work, we attempted to determine the most feasible initiation mechanisms for olefin metathesis catalysed by the MoO_x/SiO_2 [6] and WO_x/SiO_2 systems, taking into account the possible participation of the surface silanol groups.

Computational models and methods. Cluster models based on the periodic amorphous structure of dehydrated silica surface [7] or β-cristobalite structure were built to represent the MoO_x/SiO_2 [6] and WO_x/SiO_2 catalysts. Geometry optimization on the PBE0/def2-SVP level was followed by PBE0-D3/def2-TZVPP single point energy calculations. The Gaussian 09 set of programs was used.

Results and discussion. A number of potential reaction pathways for generation of the molybdenum and tungsten alkylidene species from the metal oxide precursors and propene were calculated. It is shown that surface silanol groups interacting with metal species and constituting Brønsted acid sites can play a key role in reduction of the dioxo M(VI) species (M = Mo, W) to the monooxo M(IV) species by propene, through M(VI) isopropoxy species, and in subsequent formation of the M(VI) isopropylidene species. An alternative activation pathway avoiding the reduction step is also possible. The reactivity of the metal oxide sites is significantly affected by their geometry and the local structure of silica. The proposed initiation mechanisms are kinetically preferred over non-silanol-assisted formation of the active sites. They are also in line with the reported experimental data [3-5,8]. The predicted activation barriers for the generation of the W alkylidene species are higher than in the case of the Mo alkylidene sites. This is consistent with the fact that a higher temperature is required for olefin metathesis catalysed by the WO_x/SiO_2 system, compared to the MoO_x/SiO_2 catalyst.

Acknowledgments
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Analysis of the Adsorption Rate on Catalysts for Ammonia Synthesis

Simon I. Hansen[1], Anker D. Jensen[1] and Jakob M. Christensen[1*]

[1]*Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark*

[*]*jmc@kt.dtu.dk*

Keywords: Haber-Bosch, Iron catalyst, Adsorption/desorption kinetics

Introduction.

The synthesis of ammonia is an important chemical process, but despite the maturity of the Haber-Bosch technology, the process is not fully understood. It is widely accepted that the rate determining step is the dissociative breaking of the N≡N triple bond [1-2]. However, studies have shown that an H_2/D_2 isotope effect exists, where D_2 gives a three-four times faster reaction rate than H_2 [3-4]. This is interesting since H_2 is not part of the rate determining step in the dissociative mechanism. Thus, a deeper understanding of the dissociative N_2 adsorption is necessary in order to clarify these discrepancies in the mechanism.

Experimental

An iron-based catalyst promoted with K and Al was used to carry out experiments on N_2 adsorption. The catalyst particles (150-300 µm) were placed in a glass-lined packed bed U-tube reactor with the adsorption carried out in a 100 NmL/min flow at 673 K, 1 bar with 25% N_2 and varying H_2 content (balance Ar). The adsorption times were varied by applying a quenching method developed in our research group [5]. N_2-TPD with a 2 °C/min ramp was then performed to analyze the surface coverage. The data were modelled to describe the adsorption and desorption rates of nitrogen.

Results and discussion

The model includes a quadratically decreasing heat of adsorption with increasing coverage on the basis of electrostatic arguments, and the validity of this dependence has been verified by comparison with experimental data reported in the literature [6]. The model was fitted to experimental TPD data in order to obtain an expression describing the ad- and desorption rates of nitrogen. The model fit is shown in Figure 1 along with a comparison with previously reported data on N_2 desorption from Fe(100) [7].

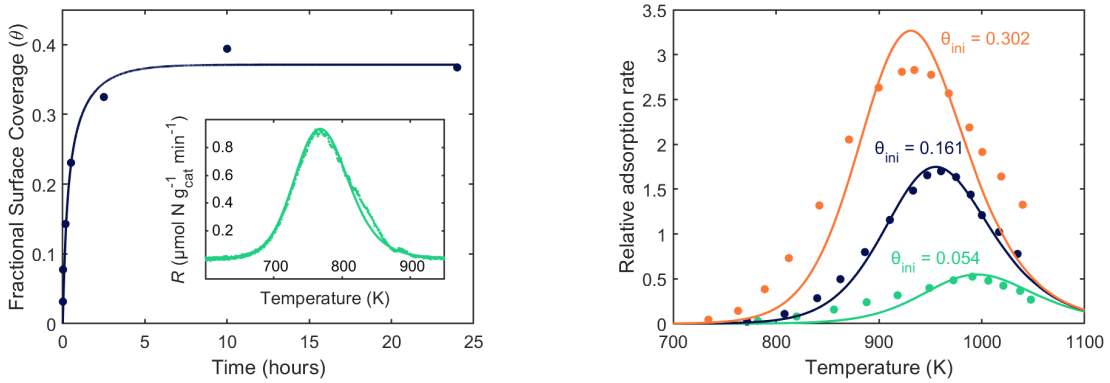

Figure 1. Left: Experimental and fitted fractional coverage of N as a function of adsorption time. Insert: TPD after adsorption at 10 hours. Right: The fitted model compared to previously reported N_2 TPD data from Fe(100) [7].

Acknowledgments

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TiO_2-supported Au Nanoparticles for Photocatalytic H_2 Evolution: A Computational Study

Aparna Harshan[1*], Tangui Le Bahers[1], and Carine Michel[1]
[1] *ENS Lyon, CNRS UMR 5182, Laboratoire de Chimie, 69364 Lyon, France.*
[*] *aparna.harshan@ens-lyon.fr*

Keywords: Core-shell nanomaterials, heterogeneous catalysis, DFT, TiO_2, gold

Introduction. Surface-supported gold nanoclusters are of increasing interest in heterogeneous catalysis due to the possibility to design unique and efficient photocatalysts by adapting the structure and complexity of the reactive interface. Recent experimental studies by Ghazzal and co-workers [1,2] have demonstrated that core-shell SiO_2@Au@TiO_2 nanostructured photocatalyst shows increased photocatalytic hydrogen production efficiency for low amount of gold nanoparticle loading. To understand the enhanced reactivity of these core-shell catalysts, computational methods are applied to simulate the electronic structural properties of the nanostructures. The study to be presented here will focus on the effect of size, shape, and structure in determining the electronic structure of Au nanoparticles on TiO_2(101) surface, which in turn influences the catalytic efficiency.

Methodology. Electronic structure calculations are performed using the open source software package CP2K with the dispersion corrected generalized gradient approximation (GGA) and Hubbard-*U* potential correction. Known geometries of stable gold nanoclusters (Au_n for n = 13, 19, 28, 32, 38, 55, …) will be used for adsorption on TiO_2(101) surface for generating the catalyst structures. Gold nanoparticles sandwiched between TiO_2 layers and embedded in thin TiO_2 shell will also be studied and the atomic charge density and projected density of states analysis will be used to compare the catalytic activities of the TiO_2(101) layer vs core-shell nanostructure.

Results and discussion. The density of states at the Fermi level is expected to change with variations in shape, size and orientation of nanoclusters [2]. Previous results from similar systems have shown that the charge density on metal nanoclusters can affect the selectivity of overall water splitting [3]. The electronic structure calculations using periodic density functional theory methods are underway for the Au_n:TiO_2 systems, and the results are expected to identify the active sites and explain the experimental observations regarding the photocatalytic activity of core-shell nanostructures. In addition to the size of the nanocluster, the shape and thickness of the surface will also be studied for simulating the experimental conditions.

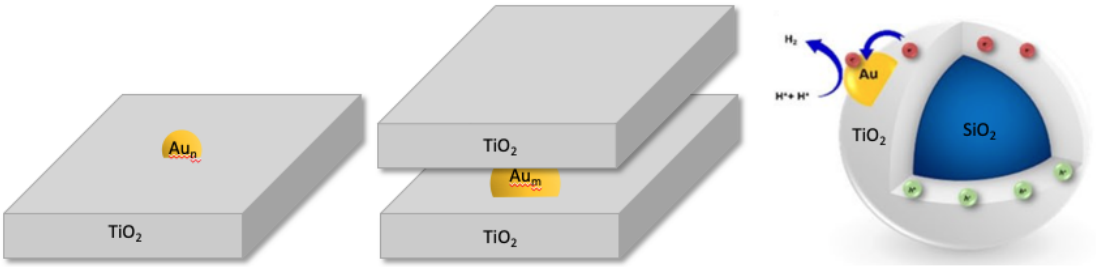

Figure 1: Systems of interest. Au nanoparticles of different sizes on different TiO_2(101) surfaces

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Mechanistic Insights into the Ru-Catalyzed Hydrogenolysis of Methanol

Nina M. Sackers,[1] Julia Nikodemus,[1] Regina Palkovits,[1] Philippe Sautet,[2,3] Peter J. C. Hausoul[1*]

[1] Chair of Heterogeneous Catalysis and Technical Chemistry, RWTH Aachen University, Germany
[2] Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, United States
[3] Department of Chemistry and Biochemistry, University of California, Los Angeles, United States
* E-mail: Hausoul@itmc.rwth-aachen.de

Keywords: Periodic density functional theory (DFT), Hydrogenolysis, Ruthenium, Methanol

Introduction.

Polyols from lignocellulosic biomass are a promising alternative to chemicals from fossil resources. Their conversion to short-chained polyols offers a variety of applications in chemical and pharmaceutical synthesis as well as food industry. However, despite numerous kinetic studies the mechanism of hydrogenolysis of these polyols is still not fully understood.[1,2] Therefore, the decomposition of the C_1 alcohol methanol was investigated as a simple model compound for mechanistic insights into the surface-catalyzed reaction.

Experimental/methodology.

Periodic DFT calculations were carried out using VASP, with the PBE exchange-correlation functional within the generalized-gradient approximation (GGA) and complemented by the Grimme D3 correction with BJ damping to account for dispersion.

Results and discussion.

The reaction mechanism to methane on a Ru(0001) surface was elucidated under realistic reaction conditions including solvation effects and coverage of the catalyst surface. A modeling of the catalyst surface revealed that the Ru surface covered with hydrogen is the most stable system. On the H-saturated Ru surface, the pathway via O H formation of the intermediate CH_2O and subsequent C O cleavage is the most favorable (Figure 1, x-xi). This study emphasizes the importance of modeling reactions under realistic conditions to obtain results that are more accurate.

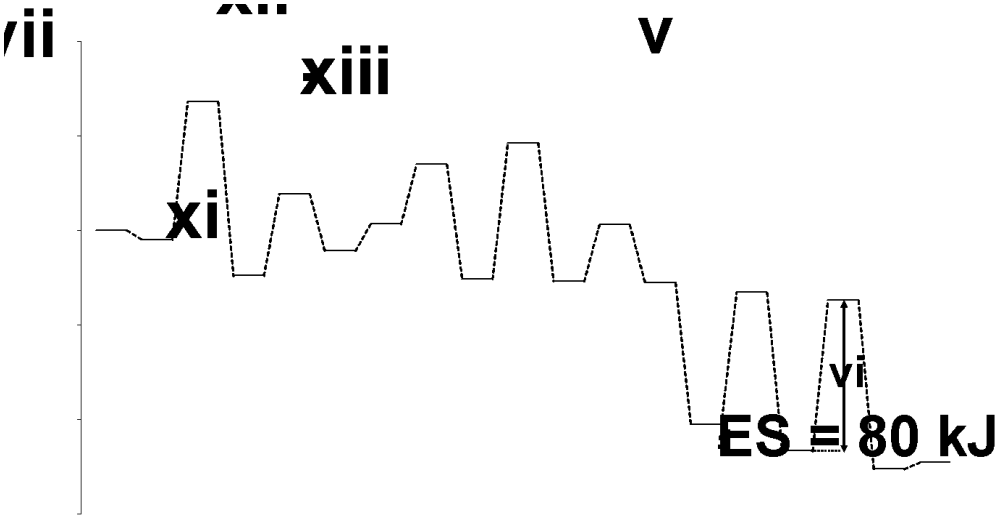

Figure 1. Decomposition of methanol to methane and water on a hydrogen covered Ru surface.

Acknowledgments

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Mechanism of NH_3 Synthesis on Fe_3Mo_3N

M. D. Higham[1,2*], Constantinos D. Zeinalipour-Yazdi[3], Justin S. J. Hargreaves[4], C. Richard A. Catlow[1,2]

[1]*University College London, London, U.K.*

[2]*Research Complex at Harwell, Rutherford Appleton Laboratory, Oxon., U.K.*

[3]*University of East London, London, U.K.*

[4]*University of Glasgow, Glasgow, U.K.*

**corresponding author: m.higham@ucl.ac.uk*

Introduction. Ammonia (NH_3) synthesis is an essential yet energy-demanding industrial process[1][2]. Hence, there is a need to develop NH_3 synthesis catalysts that are highly active under milder conditions[3]. Metal nitrides are promising candidates, with the η-carbide structured Co_3Mo_3N having been found to be more active than the industrial Fe-based catalyst[4][5]. The isostructural Fe_3Mo_3N catalyst has also been identified as highly active for NH_3 synthesis[6]. Recent experimental work has also suggested that promotion of Fe_3Mo_3N by chromium can enhance activity. In the present work, we apply computational techniques to investigate the catalytic ammonia synthesis mechanisms in Fe_3Mo_3N[7], which we compare and contrast with the previously studied Co_3Mo_3N[8-15].

Methodology. Plane-wave Density Functional Theory (DFT) as implemented in the VASP code was applied to investigate surface N vacancy formation in Fe_3Mo_3N, and two distinct ammonia synthesis mechanisms. In line with the previous studies on Co_3Mo_3N, a thin-film 2x2 surface supercell interleaved by 30Å of vacuum was used to model the Fe_3Mo_3N surface. The revised PBE XC functional was used throughout in conjunction with the D3 dispersion correction. Inner electrons were replaced with PAW, with the valence states expanded in plane waves up to a cut-off of 650 eV. A Γ-centred (4x4x1) Monkhorst-Pack k-point sampling mesh was used to sample the Brillouin zone. Electronic self-consistency was deemed to have been achieved for total energies converged to within 10^{-5} eV. All structures were optimised until atomic forces were converged to within 0.01 eVÅ. Transition states were identified using the climbing image nudged elastic bands (CI-NEB) and dimer methods, with vibrational analysis confirming that a saddle point had indeed been located.

Results and Discussion. The calculations reveal that whilst N vacancy formation on Fe_3Mo_3N is experimentally found to be more thermodynamically demanding than for Co_3Mo_3N, the calculated formation energies are comparable, suggesting that surface lattice N vacancies in Fe_3Mo_3N could facilitate NH_3 synthesis. N_2 activation was found to be enhanced on Fe_3Mo_3N compared to Co_3Mo_3N, for adsorption both at and adjacent to the vacancy. The calculated activation barriers suggest that, as for Co_3Mo_3N, the associative Mars van Krevelen mechanism affords a much less energy-demanding pathway for ammonia synthesis, especially for initial hydrogenation processes. It is intended that the present work will inform future studies investigating quaternary nitride systems and the role of Cr-promotion in Fe_3Mo_3N.

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Distance effect in bifunctional metal-acid catalysis

Kang Cheng,[1,2*] Ye Wang,[1] Krijn P. de Jong[2]

[1]*State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China*
[2]Materials Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, 3584 CG Utrecht, Netherlands.
**Corresponding Author: kangcheng@xmu.edu.cn*

Keywords: Bifunctional catalysis, shape selectivity, C1 chemistry, proximity, hydrocarbon chemicals

Introduction. Bifunctional catalysts composed of metal (oxide) and zeolites have been widely applied in the catalytic conversions of C1 molecules, short-chain hydrocarbons, and biomass-based feedstock.[1,2] The performance of bifunctional catalysts is influenced not only by the physical and chemical properties of the metal and zeolite but also by the distance between them. The distance factor also affects the catalyst stability, regeneration, and recovery of the spent catalyst. However, up to now, deep investigation and understanding of the distance factor for bifunctional catalysis are still lacking.

Results and discussion. We have investigated the distance-dependent performances from the aspects of the accessibility of functional sites, the local concentration of intermediates, and the transfer mechanism of reaction intermediates.[3-5] It is noteworthy that under harsh reaction conditions of high temperature, exothermicity, reduction, and the presence of water, metals are highly prone to migrate into the zeolite channels thus poisoning the zeolite.[6] Sometimes, this phenomenon was superficially attributed to the speculative distance effect. For the hydrogenation of CO/CO_2 to olefins by oxide-zeolite catalysts excluding metal migration, we found that gaseous methanol as an intermediate can diffuse fast and randomly between the dual active sites and therefore is not sensitive to the distance factor. In contrast, for CO/CO_2 to aromatics, metal oxide and zeolite must be integrated closely because the last aromatization step requires the fast removal of hydrogen species through the oxide-zeolite interface (Figure 1). Our work not only provides insights into emerging metal−acid catalysis for C1 chemistry but also guides the rational arrangements of functional sites and the design of reactor shapes for specific tandem reactions.

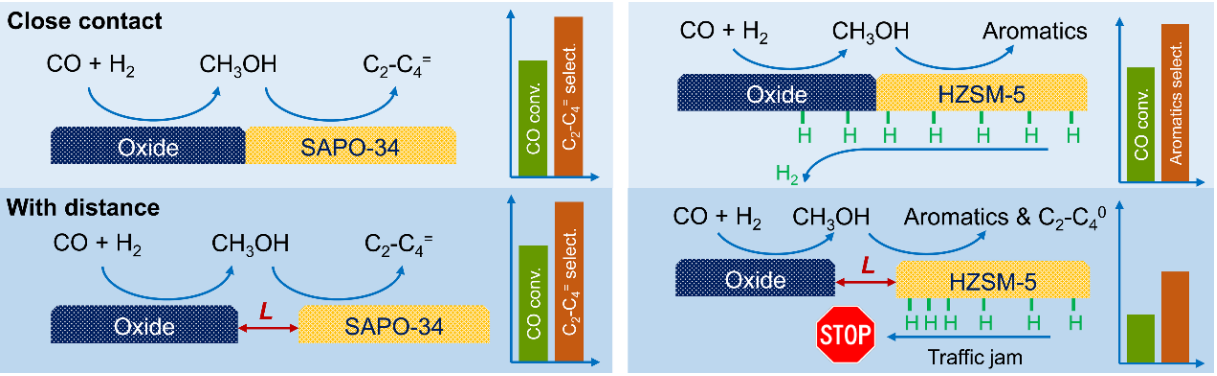

Figure.1 Distance effect of bifunctional catalysts on the performance of syngas to olefins and aromatics.

Acknowledgments

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Kinetic & mechanistic study of the complete oxidation of volatile organic compounds (VOCs) on Co_3O_4 catalysts

Y. Georgiou[1], N. Apostolopoulos[1], P. Dimitropoulos[1], M. Smyrnioti[1], C. Zhang[2], A.M. Efstathiou[2], T. Ioannides[1,*]

[1] *Foundation for Research and Technology-Hellas, Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Patras, Greece*
[2] *Chemistry Department, University of Cyprus, Nicosia, Cyprus*
E-mail: theo@iceht.forth.gr

Introduction. Catalytic oxidation of volatile organic compounds (VOCs) is an important reaction for abatement of VOC emissions from industrial sources. Transition metal oxides, such as Co_3O_4, are active catalysts for VOC oxidation and it is generally accepted that the reaction takes place via a redox (Mars-van Krevelen) mechanism, whereas the VOC gets oxidized by surface lattice oxygen leading to reduction of the catalyst surface which is subsequently reoxidized by gaseous oxygen closing the cycle [1]. In such a simplified mechanism, the kinetics of the surface reoxidation step are independent of the type of VOC and, as a consequence, kinetic analysis of the oxidation of various VOCs should result in identical rate constants for surface reoxidation regardless of the VOC type. The validity of this hypothesis was scrutinized in the present work by a kinetic and mechanistic study of oxidation of propylene, butane and toluene over two Co_3O_4 catalysts differing in specific surface area by almost two orders of magnitude.

Experimental/methodology. The prepared Co_3O_4 catalysts were characterized by SEM, PXRD, XPS, H_2-TPR, Raman spectroscopy and N_2 physisorption. Kinetic measurements were performed at four different temperatures as a function of VOC and oxygen partial pressures. The interaction of VOCs with the catalyst surface was investigated by temperature-programmed desorption (TPD, helium carrier gas) and surface reaction (TPSR, O_2/He carrier gas) following adsorption of the respective VOC at room temperature. Experiments of transient oxidation of carbonaceous species deposited after VOC reaction with lattice oxygen were also carried out aiming to probe differences in the rates and amounts of carbonaceous species deposited and oxidized by lattice oxygen or gaseous oxygen for the two Co_3O_4 catalysts.

Results and discussion. The two Co_3O_4 catalysts were of pure spinel oxide phase with similar Co^{2+}/Co^{3+} surface atomic ratios and had specific surface areas of 77 and 2.4 m^2g^{-1}, respectively. The kinetic behavior could be described in all cases by a Mars-van Krevelen rate expression, albeit with a reaction order of n~0.25 with respect to O_2 partial pressure, which does not have an obvious physical meaning. In addition, the determined kinetic rate constant for the surface reoxidation step differed significantly among the examined VOCs, which implies that the Mars-van Krevelen rate expression could be considered as an empirical description of catalyst behavior with no direct mechanistic relevance. The kinetic observations are discussed in the light of the extensive transient studies carried out in the present work which provided mechanistic information of the surface processes during VOC oxidation over Co_3O_4 catalysts towards the development of a relevant mechanistic model for this reaction.

Acknowledgments
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DFT study of acetaldehyde (AcH) and methyl acetate (MeOAc) formation on $HCo(CO)_4$ catalyst

J. Jelic[1], Kalim A. Sheikh[1], Thomas A. Zevaco[1], Felix Studt[1]

[1]*Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, 76131 Karlsruhe , Germany*

jelena.jelic@kit.edu

Introduction.

Acetaldehyde dimethyl acetal (AADMA) is a promising substance for the synthesis of pharmaceuticals, fragrances and can be efficiently used as a diesel additive to increase the cetane number. Not only used as a raw material, it is also an important intermediate for the synthesis of various oxygen-containing organic materials, such as higher acetals, resins, solvents and adhesives. The direct synthesis from CO, H_2, and methanol has not been studied extensively, and reports on the heterogeneously catalyzed synthesis of AADMA from methanol and syngas are scarce. Here we present a DFT study on the formation of acetaldehyde (AcH) and methyl acetate (MeOAc) on the $HCo(CO)_4$ catalyst to support the experimental results.

Experimental/methodology.

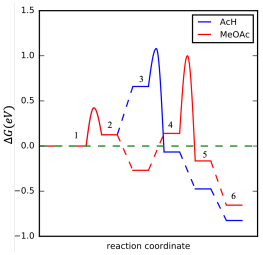
Density Functional Theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP) in connection with the Atomic Simulation Environment (ASE). The Bayesian Error Estimation Functional with van der Waals correlations (BEEF-vdW) with the projector augmented wave method (PAW). The choice of the BEEF-vdW functional is motivated by its performance with respect to adsorption energies and transition states on transition metal surfaces. Due to the presence of delocalized Co d orbitals, we applied GGA+U (U = 4.0 eV) method.

Large 12x12x12A unit cells were used to represent isolated $HCo(CO)_4$ species. Transition states are obtained using constrained optimizations and Nudge elastic band (NEB) calculations. Entropic contributions to the free energy were calculated within the harmonic approximation.

Results and discussion

DFT calculations were performed to complement the experimental work and to support some assumptions regarding the mechanisms, in solution and on the surface.

As a first step, we tested the stability of a $Co_2(CO)_8$ cluster (the most stable form of cobalt carbonyl) in the presence of H_2. Upon H_2 dissociation, the $Co_2(CO)_8$ dimer became unstable and dissociated into two $HCo(CO)_4$ monomers. Barrier for the whole process is 0.86 eV. In the liquid phase, a proton transfer from the $HCo(CO)_4$ cluster to methanol can take place. Using a single MeOH molecule to simulate the process requires overcoming a barrier of 1.7 eV in the Gibbs free energy diagram. Using more than one MeOH molecule to simulate the liquid phase for easier proton transfer was necessary and we used three MeOH molecules around $HCo(CO)_4$. This significantly lowered the barrier for the $CH_3Co(CO)_4$ formation. After creation of cobalt methyl tetracarbonyl, the formation of acetaldehyde (AcH) and methyl acetate (MeOAc) was studied and compared. The results show that the barriers for both processes are of similar magnitude and that both could take place equally. Increasing the hydrogen pressure decreases the barrier to AcH formation. The formation of CH_4 as a by-product was also taken into consideration.


AcH
MeOAc
1.5
1.0
0.5
0.0
−0.5
−1.0
$\Delta G\,(eV)$
1
2
3
4
5
6
reaction coordinate

Mechanistic Insights into the Catalytic Hydrogenation of Muconic Acid in Aqueous Phase

Haseena K V[1], M. Ali Haider[*]
[1]*Indian Institute of Technology Delhi, Delhi, India*
[*]*haider@iitd.ac.in*

Keywords: Hydrogenation, Aqueous Phase, Proton Coupled Electron Transfer, Density Functional Theory

Introduction.

The transition metal catalysed hydrogenation of unsaturated functionalities, such as alkenes, primarily occurs via the Langmuir-Hinshelwood mechanism. The presence of solvents often tend to alter the conventional mechanism of hydrogenation, promoting alternate routes which are energetically more favourable.[1,2] In the present study, catalytic transfer hydrogenation (CTH) of trans,trans-muconic acid (TTMA) to adipic acid (AA) is explored in different solvents. Complete conversion is observed in the presence of water in 120 mins reaction time, whereas reduced conversion is observed in THF and cyclohexane. It is hypothesised that the hydrogen-bonded network of water molecules assists the hydrogen transfer to the C=C bond via a proton coupled electron transfer mechanism (PCET). Herein, density functional theory (DFT) simulations are employed to capture the energetics of the possible reaction pathways in solvents to develop a mechanistic understanding of the hydrogenation reaction.

Experimental/methodology.

CTH of trans,trans-muconic acid is carried out in an Anton Paar reactor equipped with a stainless steel heating jacket and integrated pressure and temperature control system. The chromatographic analysis of the reaction mixture is performed using the HPLC supplied by Agilent Technologies (1260 infinity II series), and the compounds are separated on a Hiplex-H column. Plane-wave DFT calculations, as implemented in Vienna ab-initio Simulation Package (VASP 6.2.0) is employed to study the mechanism of hydrogenation on different facets of a Pd surface. An explicit solvation model is used to simulate the solvent environment.

Results and discussion.

The hydrogenation reaction of TTMA is performed using Pd/C (10%) catalyst and formic acid as hydrogen source at 70°C and autogenous pressure. Nearly 100% conversion with 82% selectivity to AA is observed in water in 120mins (Table 1). Appreciable conversion is observed in polar protic solvents such as ethanol and methanol (Table 1). However, in THF, the activity is seen to reduce to half, and in cyclohexane, the conversion drops to 9% (Table 1). A detailed mechanistic study is therefore carried out using DFT simulations to understand the observed shift in conversions in different solvents. Figure 1. Shows the most stable binding mode of TTMA on Pd(111) and Pd(100) surfaces. The activation barriers for the hydrogen transfer in the presence of explicit water would be captured to develop mechanistic insights into the hydrogenation pathways.

Table 1. Effect of Solvents in CTH of TTMA

S. No	Solvent	Conversion (%)	Adipic Acid (%) Yield
1	Water	100	82
2	Ethanol	98	87
3	Methanol	88	-
4	THF	50	-
5	Cyclohexane	9	-

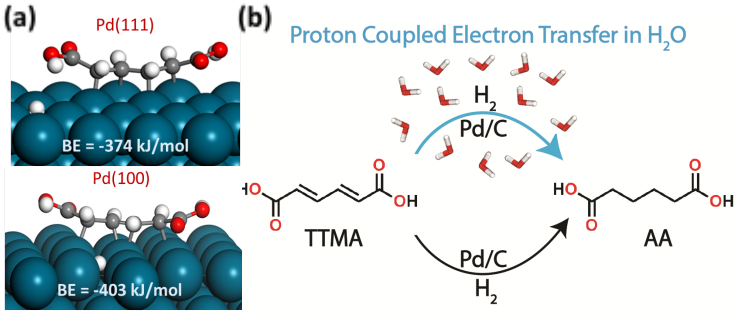


Figure 1. (a) Most stable binding mode of TTMA on Pd(111) and Pd(100) surfaces (b) Reaction scheme for TTMA hydrogenation using Pd/C catalyst.

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The efficiency of nickel-containing catalysts for the transformation of carbon monoxide and methane into graphite-like carbon allotropes

A. Kaporov*, O. Shtyka, R. Ciesielski, A. Kedziora, W. Maniukiewicz, J. Albinska, T. Maniecki

Institute of General and Ecological Chemistry, Faculty of Chemistry, Lodz University of Technology, 116 Zeromskiego St., 90-924 Lodz, Poland
**artem.kaporov@dokt.p.lodz.pl*

Keywords: nickel-containing catalysts, Boudouard reaction, methane cracking, nanostructured carbon allotropes, greenhouse gases transformation

Introduction. It is widely recognized that greenhouse gas emissions, such as CO2 and CH4, are alarmingly high and cause serves damage to the environment despite international efforts to mitigate emissions of these gases [1]. In this regard, lots of scientific efforts have been put into the investigation of the possibility of conversion of them into valuable materials, such as carbon nanotubes, graphene, fullerenes, diamonds, etc., due to their cheapness, abundance, and relative safety [1-5]. One specific process that utilizes these gases is the dry methane reforming (DRM), during which side reactions (i.e., the Boudouard reaction and methane cracking) occur to form different types of carbon deposits [6-8]. The presented project aimed to study the effect of the type of catalytic support (CaO, Al2O3, MgO) on the performance of Ni catalysts in the Boudouard reaction and methane cracking.

Experimental/methodology. Ni catalysts supported on CaO, Al2O3, and MgO were prepared using the impregnation method. The catalytic measurements were performed using continuous flow reactor under atmospheric pressure at 450 and 700 °C for the Boudouard reaction and methane cracking, respectively. The gases composition was measured using online gas chromatographs with thermal conductivity detectors (TCD). The physicochemical properties of samples were analyzed using atomic adsorption spectroscopy (AAS), Brunauer-Emmett-Teller method (BET), temperature-programmed reduction/oxidation and desorption of NH3 and CO2 (TPR, TPO, NH3- and CO2-TPD), total organic carbon analysis (TOC), and X-ray diffraction (XRD).

Results and discussion. The experimental results showed that graphite-like carbon nanotubes were mainly formed on the surface of catalysts irrespectively of the investigated process. Also, it was evident that, the amount of carbon deposit depended on the physicochemical properties of catalytic systems, mainly, susceptibility to the reduction and concentration of acid-base sites. In particularly, the highest amount of graphite-like carbon was observed on the surface of Ni/CaO and Ni/Al2O3 (15-20%). These catalytic systems characterized by highest concentration of strong acid-base sites and relatively good reducibility. At the same time, the lowest carbon content was determined in the case of Ni/MgO (5-10%). This catalyst did not undergo complete reduction due to the formation of NiO-MgO solid solution. The mechanisms of formation of graphite-like carbon species during the Boudouard reaction and methane cracking were suggested.

Acknowledgments
This research has been completed while the first author was the Doctoral Candidate in the Interdisciplinary Doctoral School at the Lodz University of Technology, Poland (A.K. (Artem Kaporov)).

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Automated Multiscale Simulation Environment – what that's about?

Kamila Kaźmierczak,[1,*] Albert Sabadel-Rendón,[2] Santiago Morandi,[2] Florian Euzenat,[3] Daniel Curulla-Ferré,[1] Núria López[2,*]

[1] *TotalEnergies OneTech Belgium, TOTB, Feluy, Belgium*
[2] *Institute of Chemical Research of Catalonia, ICIQ, Tarragona, Spain*
[3] *TotalEnergies Research and Technology, TRTG, Gonfreville, France*
[*] *Corresponding Authors: nlopez@ICIQ.ES, kamila-maria.kazmierczak@totalenergies.com*

Keywords: heterogeneous catalysis, multiscale approach, DFT, automatization

Industrial production of fuels and chemicals would not be possible without catalysts. Different processes require different catalytic materials though. With the now changing reality, where new feedstocks are developed, an efficient way to discover materials active and selective in given reaction is needed. Over the last years, the materials' performance assessment was done at the molecular scale using Density Functional Theory (DFT) calculations. This approach, however, does not give any insight on the performance of the material under various reaction conditions. To gain it, we need to extend our studies on additional time and length scales.[1]

Together with our academic partners from Institute of Chemical Research of Catalonia (ICIQ) in Tarragona (Spain) we approached this problem. Multiscale modelling workflow, together with Automated Multiscale Simulation Environment (AMUSE) tool, was created to address catalytic reactions on multiple scales.[2]

The starting point for the workflow are DFT calculation results. They can be produced from scratch in house, or they can be retrieved from databases, like ioChem-BD,[3] or existing literature. Then, they are automatically treated with the AMUSE tool to: i) retrieve the molecules structures and energies, ii) transform the structures into molecule graphs, iii) find the connections between these graphs and build the full reaction network, iv) ascribe the appropriate reaction energies to the elementary steps. These previous steps enable to proceed to microkinetic modelling. This approach allows us to get first insight, comparable with the experimental output, into catalysts' performance. We can anticipate the material efficiency, in terms of conversion and selectivity, under various temperature, pressure, and substrates concentration conditions. That can serve as the first filter for the promising materials selection. Yet, to be even closer to the reactor scale physics, we need to include transport phenomena, which is possible with Reactive Fluid Dynamic calculations.

For benchmark the workflow was tested with two reactions: CO_2 hydrogenation to methanol on Pd/In_2O_3, and isopropanol dehydrogenation on Co(0001) and Co(11-20) facets. The obtained simulation results are in line with the experimental observations, by which the proof of concept was achieved.

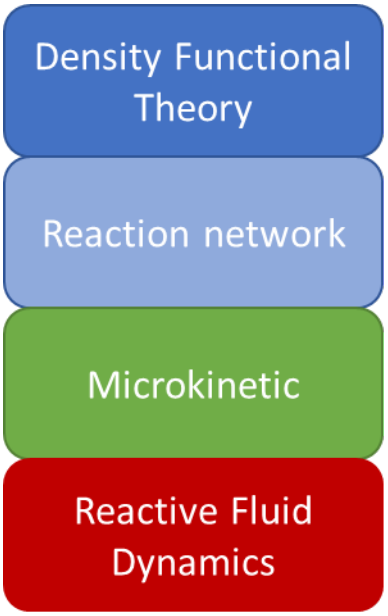

Figure 1. Schematic illustartion of our automated multiscale modelling workflow for heterogeneous catalysis.

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Decoding the selectivity control of Zeolitic-Imidazolate Framework-8 in the conversion of furanics through DFT

T.-H. T. Le[1*], M. A. Ortuño[1]

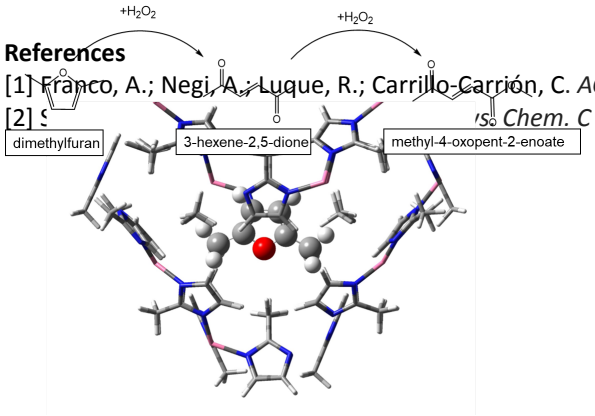
[1]*Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain*
[*]*hiep.le@rai.usc.es*

Keywords: furanics, metal-organic frameworks (MOFs), selectivity control, DFT.

Introduction. Biomass valorization to generate green fuels and value-added chemical products is a promising way to mitigate the demand on fossil fuels and diversify feedstocks. The context of biomass-derived furanics dominates the research because of their intrinsic reactive nature which connects between aliphatic and alicylic compounds. In upgrading processes, ring-opening oxidations are particularly sensitive and difficult to control. A series of side-products could be obtained along with the target product, thus selectivity control is necessarily required. In the concept of heterogeneous catalysts, metal organic-frameworks (MOFs) are promising porous materials with highly catalytic properties for biomass conversion. Recent research demonstrated that the zeolitic-imidazolate framework (ZIF-8) MOF can act as selectivity mediator for the conversion of dimethylfuran (DMF) to 3-hexene-2,5-dione.[1] A reaction mechanism was proposed, however, a comprehensive study on how ZIF-8 controls the product selectivity was not fully addressed. To tackle these issues, we apply computational simulations at atomic level.

Methodology. Calculations were performed at periodic Density Functional Theory (DFT) level using the Vienna Ab-Initio Simulation Package (VASP) 5.4. The PBE exchange-corelation density functional was employed. NCIPLOT program was used to reveal non-covalent interaction between reactants, intermediates, products, and ZIF-8. An automatic search for efficient binding sites on ZIF-8 was carried out by xTB and CREST in combination with GFN-FF.[2] All values correspond to Gibbs energies at 333.15 K.

Results and discussion. We report the thermodynamics reaction pathway of DMF conversion with and without ZIF-8. After 3-hexen-2,5-dione is formed, the next step involving a second H_2O_2 molecule affects selectivity by promoting overoxidation side-processes. To the best of our knowledge, this is the first mechanistic study on interactions between large adsorbates and bulk ZIF-8 at periodic model. With automated searching tools for geometry structures, we systematically search the configurational space to obtain the most stable binding sites on ZIF-8. Unraveling the main interactions between intermediates and MOFs provides atomistic information on how and why ZIF-8 promotes selective for DMF conversion. With that knowledge at hand, other MOFs could be test to further improve the process.



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Changes of Oxygen Species on the Surface of Manganese Catalysts and their Effects on Acetaldehyde Ozonation

Yoon-Kyoung Lee[1], Eun-Chae Doh[1], Jun-Pyo Cho[2], JiHyeon Song[1*]

[1]*Sejong University, Seoul, South Korea*
[2]*FST corp., Gyeonggi-do, South Korea*
[*]*songjh@sejong.ac.kr*

Keywords: Manganese catalysts, Oxygen species, Acetaldehyde, Ozonation

Introduction.
Acetaldehyde is one of the volatile organic compounds (VOCs) that requires stringent regulations. Catalytic oxidation is commomly applied to reduce and control acetaldehyde emissions. In this study, an oxidation reaction of acetaldehyde using manganese catalysts and ozone was studied at room temperature. Active oxygen species formed on the surface of the catalyst are known to have high oxidizing power resulting in an increase of the oxidation rate. Therefore, the support of the catalysts was pretreated with strong acid to change the specific surface area and the ratio of oxygen species, and the effect of the surface modification on the acetaldehyde ozonation was investigated.

Experimental/methodology.
A cordierite support in a honeycomb shape was applied in this study, and its suface was pretreated with strong acid for 0, 30, 60, and 90 minutes. After the surface modification, manganese oxide catalysts were preapred at 5 wt% using the wet impregnation method. The oxygen species form on the Mn catalysts surface was confirmed through X-Ray Photoelectron Spectroscopy (XPS), which indicated O_{vac}, an oxygen vacancy and O_{lat}, a lattice oxygen in a manganese oxide bond.
The Mn catalyst was packed in a stainless-steel column, and the ozone oxidation efficiency of acetaldehyde was tested in the column study at the space velocity of 3,600 hr^{-1}. The total flow rate in the column was fixed at 3 L/min by adjusting a mass flow controller. The concentration of gaseous acetaldehyde in an air stream was set to be 100 ppm, and the molar ratio of ozone/acetaldehyde (5:1) required for the complete oxidation of acetaldehyde was selected as a reference condition.

Results and discussion.
The specific surface area and the oxygen vacancies (O_{vac}) on the surface of the Mn catalysts were compared as the acid pretreatment time changed. At the acid-pretreatment times of 0, 30, 60, and 90 minutes, the average specific surface areas were found to be 0.1, 35.6, 82.4, and 104.3 m^2/g, respectively. The analyses of the oxygen species on the surface of Mn catalysts revealed that the ratio of O_{vac} were 84%, 86%, 88%, and 92%, respectively. As result, the specific surface area and the O_{vac} of the Mn catalysts increased proportionally with increasing the acid pretreatment time.
The column study showed that the average ozone removal rates were 11%, 34%, 47%, and 54% at the acid pretreatment times of 0, 30, 60, and 90 minutes, respectively. In addition, the average acetaldehyde degradation rates were 49%, 98%, 100%, and 100%. Therefore, the higher the O_{vac} ratio on the Mn catalyst surface, the higher the ozone activity, and therefore, the acetaldehyde removal efficiency was also improved. It is necessary to optimize the pretreatment method and to investigate the oxidation mechanisms of acetaldehyde on the various Mn catalysts with different oxygen species.

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Ethanol conversion to 1-butanol by heterogeneous catalysis using Li-Al metal mixed oxides dopped with transition metal

Jan Malina[1*], Martin Hájek[1], Karel Frolich[1]

[1]University of Pardubice, Faculty of Chemical Technology, Department of Physical Chemistry, Pardubice, Czech Republic
*jan.malina@student.upce.cz

Keywords
Guerbet alcohols, Heterogeneous catalysis, Mixed metal oxides, Cu-Li-Al

Introduction

This work is focused on the transformation of ethanol to more valuable chemical compounds via heterogeneous catalysis in a flow reactor. One of the desired products is butanol, which is important chemical compound, which can be used such as solvent or as feedstock for production of other chemical compounds, e.g., hexanol, butyl acrylate, iso-butene (additive to polymers). The transformation of ethanol to butanol can be achieved by the Guerbet reaction, which is self-condensation of two primary alcohols to the beta-alkylated dimer alcohol and consist of four steps [1].

Mixed metal oxides of lithium, aluminum, and transition metal (copper) were used as heterogeneous catalysts for the Guerbet reaction [2]. Lithium, aluminum mixed metal oxides from layered double hydroxides precursors (LDH) were chosen as one of the possible alternatives to more common magnesium, aluminum mixed oxides. The influence of different amount of transition metal in mixed oxides on ethanol transformation was studied and catalytic data were obtained, i.e., conversion of ethanol and selectivity of reaction to butanol (and other products). Mixed metal oxides were also deeply characterized by several experimental techniques.

Experimental/methodology

Mixed metal oxides were obtained via decomposition of LDH precursors prepared by the urea method (co-precipitation with urea) in a batch reactor with reflux condenser at atmospheric pressure and 105 °C. Alumina, lithium and copper nitrates were weighed at specified molar ratios of metals and were dissolved in redistilled water. Solution of metal ions was transferred into batch reactor and heated to 105 °C and urea was added to adjust pH and start the co-precipitation. Obtained LDH precursors were calcinated to mixed metal oxides and characterized by various methods: ICP-OES, X-ray diffraction, N_2-Physisorption, TPR and TPD. Catalytic studies were performed in a micro flow reactor with catalyst bed, at various temperatures (300–400 °C) in a mixture of 10 % ethanol and helium gas and atmospheric pressure.

Results and discussion

The properties of mixed oxides were determined for better understanding of the catalytic activity. Characterization data were statistically analyzed and correlated with catalytic data to determine the most suitable composition of heterogeneous catalysts for the reaction. Addition of transition metal had a positive influence on the ethanol conversion, on the other hand higher basicity and acidity had positive influence on butanol selectivity. Tuning of heterogeneous catalysts for the Guerbet reaction can provide relatively simple, cheap, and sustainable method of production not only bio-butanol.

Acknowledgments
This work was supported by the University of Pardubice, Czech Republic, project SGS_2022_007.

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Kinetic Modeling of Anisole Hydrodeoxygenation for high aromatic selectivity over Ru/TiO_2 Catalysts

Víctor Martínez Jiménez [a] *, José Antonio de los Reyes [a], Cindy García Mendoza [a]

[a] *Universidad Autónoma Metropolitana, Ciudad de México, México.*

**vimaji2302@gmail.com*

Introduction

Reaction kinetics information is crucial to determine the size of the commercial catalytic reactor and to improve the catalyst [1]. Regarding HDO kinetics of model molecules such as anisole, authors have reported three major pathways, (a) demethoxylation (DMO) [2,4], (b) demethylation (DME) [3-5], and (c) primary hydrogenation/secondary deoxygenation (HYD) [3,4]. However, there are aspects of this mechanism that remain unsettled and require further analysis. Therefore, a Langmuir-Hinshelwood-type kinetic model was proposed to describe the HDO of anisole over a Ru-based catalyst. The objective of this study is to obtain kinetic parameters that allow us to provide a quantitative framework to interpret data and to elucidate HDO reaction mechanisms for high aromatic selectivity.

Experimental/methodology

Rate expressions were derived based on a conventional Langmuir-Hinshelwood model, considering 2 types of catalytic sites: the first, where the anisole molecule and each of the products of the reaction network are absorbed (Figure 1), the second, where hydrogen is adsorbed and dissociated.

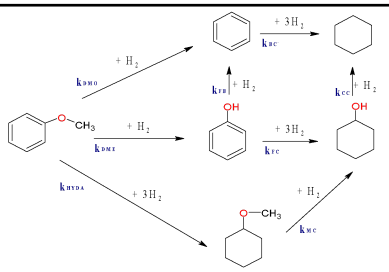

Figure 1. Anisole conversion reaction network over Ru/TiO_2 (T = 200-300 ° C, P = 30-50 bar).

The rate expression for anisole is:

$$r_A = \frac{k_A K_A C_A}{1 + \sigma K_i C_i} \quad , \quad k_A = k'_A \left[\frac{\left[\overline{K_{H_2} C_{H2}} \right]}{1 + \left[\overline{K_{H_2} C_{H2}} \right]} \right] \qquad (1)$$

Where i: represents anisole and each of the products of the reaction network.

Results and discussion

A temperature of 300ºC favored the obtention of products of interest (benzene). The formation of methylcyclohexane was not observed, thus its adsorption was neglected. From the kinetic and absorption constants calculated for each compound, benzene and cyclohexanol are the most strongly adsorbed compounds. Cyclohexanol and phenol reacted faster than the other products, cyclohexanol showed a reaction constant of 2.8 times and phenol, 2.2 times that of anisole. These values are consistent with the small yields to phenol and cyclohexanol as compared with benzene. Figure 2 shows the concentration of anisole versus WHSV. The predicted data from the proposed model gave a fair fit to the data observed experimentally for de hydrodeoxygenation of anisole over the Ru/TiO_2 catalyst.

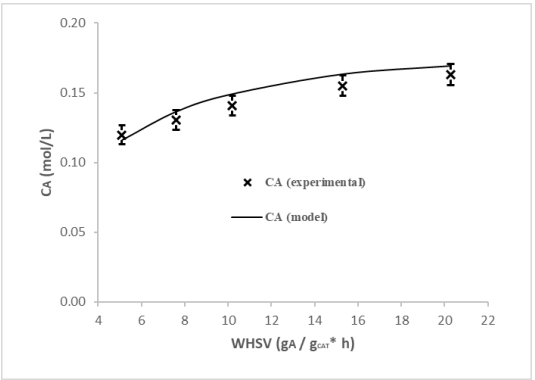

Figure 2. Comparison between the estimated and experimental data for the concentration of anisole as a function of WHSV (T = 300 ° C, P_{H2} = 40 bar).

From the estimated kinetic parameters it can be said that the DMO pathway (to produce benzene) is preferred over the DME pathway, and the conversion step of Cyclohexanol to cyclohexane is the fastest. This leads to a higher yield of deoxygenated compounds.

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First-Principles insights into the Reduction Half Cycle of the LT NH_3-SCR over Cu-CHA under wet conditions

G. Contaldo[1], M. Ferri[1], C. Negri[1], I. Nova[1], M. Maestri[1,*] and E. Tronconi[1,*]

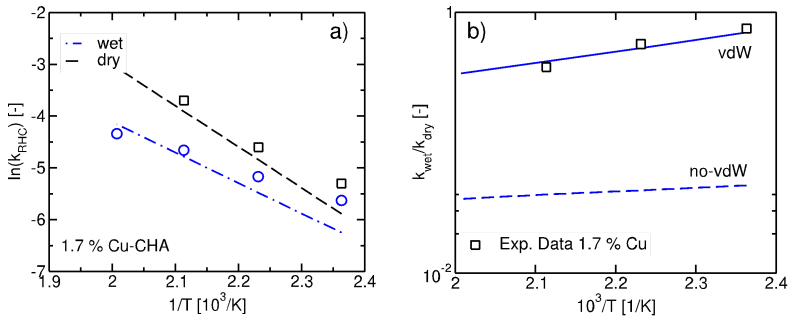
[1]*LCCP, Dipartimento di Energia, Politecnico di Milano, via La Masa 34, 20156, Milano, Italy*

[*] *matteo.maestri@polimi.it* [*]*enrico.tronconi@polimi.it*

Introduction. The NH_3-assisted selective catalytic reduction (SCR) is the leading technology for the NO_x abatement from lean burn engines. In this context, Hu et al. [1] proposed a DFT-derived mechanism for the LT reduction half cycle (RHC) under dry conditions which identifies the oxidative activation of NO to HONO as the kinetic relevant step of the reduction cascade, consistent with the experimental observations that reveal a rate proportional to NO pressure and a quadratic dependency on Cu(II). Furthermore, Gramigni et al. [2] reported that the inclusion of H_2O in this reacting system affects the thermodynamic and kinetic parameters by decreasing the apparent activation enthalpy of the RHC to half of its dry counterpart while on the other hand inhibiting the reaction rate, even with the same rate dependency with respect to the dry conditions. A clear explaination to these effects is still lacking, therefore here we examine the role of H_2O in the RHC of the NH_3-assisted SCR in order to provide a detailed mechanistic interpretation of such phenomena and improve the actual knowledge of the detailed chemistry that regulates the RHC under wet conditions.

Experimental/methodology. We performed hybrid density functional theory (DFT) calculations that account for van der Waals interactions with the Grimme D_3 method in a 12T-sites unit cell of Cu-CHA. The TS structures in wet and dry conditions are identified using the climbing-image nudge elastic band methodology (CI-NEB) in combination with statistical thermodynamic formalisms for the evaluation of entropy, enthalpy and Gibbs free energy. Vibrational frequency calculations are performed by using a finite-difference approximation of the Hessian matrix implemented in ASE.

Results and discussion. The experimental evidences reported by Gramigni et al. [2] indicate that the RHC under wet conditions follows the same kinetic scheme observed in the dry system and suggest that H_2O does not affect the dinuclear nature of Cu(II). For this reason, we introduce one H_2O molecule in the proximity of Two-P and NO inside the cage of CHA. According to our results, the presence of H_2O influences the Gibbs free energy of the kinetically-relevant TS structure producing strong enthalpic stabilization effects which result in the net decrease of the apparent activation enthalpy by 20 kJ/mol with respect to the dry case, from 62 to 42 kJ/mol, in analogy with experiments. However, the entropic penalties gained after the addition of one H_2O molecule are predominant and prevail over the enthalpic stabilization effects producing the experimentally observed inhibition of the reaction rate, blue curve in Fig.1(a). In particular, the ratio between the wet and dry rate constants is shown in Fig.1 (b) and it decreases at high temperature because in this range the entropic losses more than compensates over the enthalpic stabilization. As a result, the inhibition effects produced by H_2O on the RHC are more strongly evident when temperature increases. It is relevant to notice that such stabilization effects vanish when vdW contributions are excluded from the calculations (dashed blue line), in analogy with the catalysis by confinement effects observed in voids of molecular dimensions [3].



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Utilizing CO_2 and excess Hydrogen from FP-PEMFC System by CO_2 Methanation over Ni-La/Al_2O_3 catalyst

Cihat Öztepe[1,2], Burcu Selen Çağlayan[2,3], A. Erhan Aksoylu[1,2*]

[1]*Department of Chemical Engineering, Boğaziçi University, Bebek, Istanbul 34342, Turkey*
[2]*SNG&HydTec Lab, Science and Technology Building, Boğaziçi University, Kandilli, Istanbul 34684, Turkey*
[3]*Advanced Technologies R&D Center, Boğaziçi University, Bebek, Istanbul 34342, Turkey*
[*]*aksoylu@boun.edu.tr*

Keywords: CO_2 Utilization, CO_2 Methanation with excess H_2 from a PEMFC

Introduction. Fuel processor (FP) technology is an applicable way to produce on-site H_2 for a PEM-Fuel Cell (PEMFC) in order to overcome the difficulty of high volume need of H_2 in direct usage [1, 2]. CO_2 is produced in addition to H_2 through an FP while produced H_2 is not fully converted in a PEMFC. In this case, CO_2 methanation emerges as a plausible solution for both utilizing produced CO_2 and beneficial use of excess H_2. The main concern for this application is low H_2 concentration, therefore, low H_2/CO_2 ratio to be used as a feed for CO_2 methanation. In this study, catalytic CO_2 methanation tests are conducted over Ni-La/Al_2O_3 system at low H_2/CO_2 feed ratios via using Box-Behnken experimental design, which makes further modelling studies possible.

Experimental. Temperature, H_2/CO_2 feed ratio, La promoter loading and GHSV are selected as factors for a Box-Behnken experimental design for both experimental comparisons and possible further modelling studies in ranges of 300-400 °C, 0.5-1.5, 1%-5% and 40,000-60,000 $ml.h^{-1}.g^{-1}$, respectively. In addition to widely used performance indicators of CO_2 conversion and CH_4 selectivity, H_2 conversion is also used to compare experiments since low H_2/CO_2 is far below the ideal stoichiometry of 4.

Results and discussion. The effect of each factor is observed at minimum and maximum levels of another factor in a Box-Behnken design. Increasing temperature mostly causes a slight increase in CO_2 conversion and a slight decrease in CH_4 selectivity. H_2 conversion significantly rises with temperature at low level of La loading and high level of GHSV whereas it slightly decreases or slightly increases with an increase in temperature at other conditions. Figure 1 shows effect of the temperature as a sample demonstration. Moreover, higher H_2/CO_2 feed ratio has a significant positive effect on both CO_2 conversion and CH_4 selectivity; however, the increase in H_2 conversion in response to an increase in H_2/CO_2 feed ratio is slight. In general, CO_2 conversion, CH_4 selectivity and H_2 conversion slightly increases with increasing La loading percentage and decreasing GHSV, except low temperature comparison indicating more significant changes.

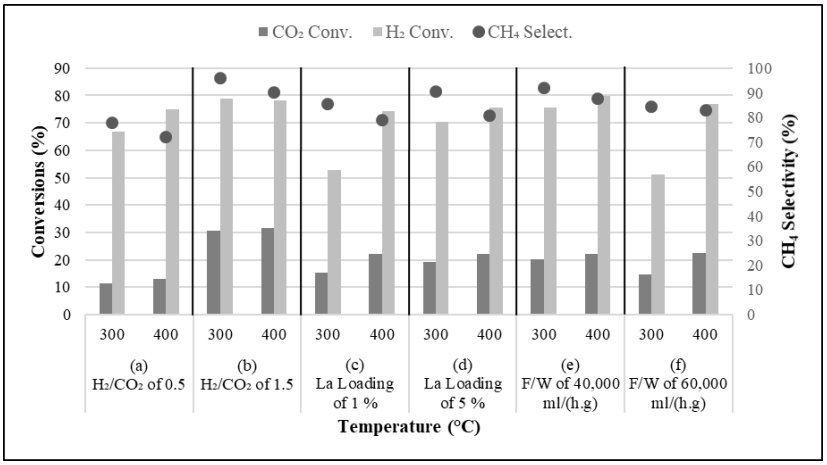

Figure 1. Effect of the temperature on CO_2 and H_2 Conversions, and CH_4 Selectivity

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Dry reforming of methane under microwave-assisted heating: *Operando* thermal analysis

J.Palomo, D. Cette, A. Urakawa*

Catalysis Engineering, Department of Chemical Engineering, Delft University of Technology, Delft, 2629 HZ, The Netherlands

* A.Urakawa@tudelft.nl

Keywords: DRM, Microwave heating, *operando* thermal analysis, Ni-catalyst.

Introduction. Dry Reforming of Methane (DRM) has attracted much attention as an effective route to convert two of the main greenhouse gases, namely methane and carbon dioxide, into syngas. Due to the high stability of methane, together with the thermodynamic limitations affecting the process, DMR has to be conducted at high temperatures. In addition, the high endothermicity of the reaction demands an intense energy supply. Furthermore, conventional Ni-based catalysts suffer severe deactivation with time on stream due to the formation of coke on the active sites of the catalyst. On the other hand, microwaves have been proved to be very efficient in driving heterogeneous catalytic reactions [1], having the interesting feature of being able to selectively heat up the solid catalyst rather than the catalyst and gas phase. In this contribution, the effect of microwave heating on DMR is analysed.

Experimental/methodology. Ni-based catalyst were prepared by incipient wetness impregnation (10 $\%_{w/w}$ Ni) of three different supports, namely: ZrO_2, Al_2O_3 and Fe_2O_3. The resulting materials were fully characterized and used catalyst in the DRM reaction, under conventional resistive and microwave assisted heating conditions. Thermal phenomena taking place in the catalyst bed were experimentally evaluated using a customized microwave system, which allows to incorporate different analytical tools under operando conditions.

Results and discussion. XRD results showed the presence of NiO crystal phases when ZrO_2 and Fe_2O_3 were used as support. In the case of Al_2O_3 supported catalyst, only Ni aluminate species were detected. H_2-TPR profiles evidenced that Ni species were reducible in all the prepared catalyst. Catalytic results (Figure 1a) showed that operation under microwave heating conditions resulted in a higher methane conversion than the one obtained using conventional resistive heating. *Operando* thermal visualization analyses, revealed a totally isothermal catalyst bed when using conventional resistive heating. On the other hand, the presence of thermal gradients and hotspots in the catalytic bed was observed under microwave-assisted heating conditions (see Figure 1b). This localized heating was a key aspect in achieving a higher methane conversion.

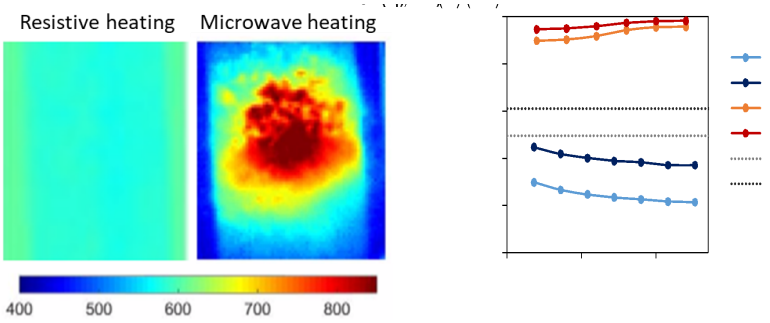

Figure 1. a) Catalytic resulst and b) IR thermography of Ni-Al_2O_3 catalyst bed, under microwave and resistive heating conditions. Reation T = 600 ºC, CH_4:CO_2 = 1, P_{CO2} = 25 %, F_{total} = 150 mL/min.

Acknowledgments

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Molecular insight into Propane dehydrogenation catalysed by Pt sub-nanoclusters on g-C_3N_4.

J. Pan[1], E. Strugovshchikov[1], A. Salom[1], J. J. Carbó[1], D. Curulla-Ferré[2], K. Kaźmierczak[2], C. Godard[1*], J. M. Ricart[1*]

[1]*Universitat Rovira i Virgili, Department de Química Física i Inorgànica, Tarragona, Spain*
[2]*TotalEnergies OneTech Belgium, Feluy, Belgium*
* cyril.godard@urv.cat; josep.ricart@urv.cat

Today, the increasing demand of propylene requires the development of more efficient ways of production, such as direct propane dehydrogenation (PDH).[1,2] Platinum-based materials are one of the most suitable catalysts for PDH due to their remarkable activity and selectivity for C-H bond breaking. However, the energetic cost of propene desorption on Pt surfaces, and the deep dehydrogenation leading to coke formation are big challenges.[3] It has been shown that the selectivity of platinum could be improved using disperse Pt small particles on different supports.[4] Herein, we present a theoretical study of PDH catalysed by platinum supported on g-C_3N_4,[5,6] from single atom catalyst[7] to small sub-nanoclusters, paying attention to the effect of cluster size on the activity and selectivity. We have also analysed the diffusion of platinum into the support.

All static calculations were performed with the Vienna Ab Initio Simulation Package (VASP) [8] using the Perdew−Burke−Ernzerhof (PBE) functional. For molecular dynamics, the in house parametrized ReaxFF reactive force field [9] was used in addition to VASP. We considered four layered slabs of the (001) g-C_3N_4 and a p(2x2) supercell. Pt atoms, dimers and trimers were situated on one side of the slab.

Pt_1, Pt_2 and Pt_3, anchored on the support, are stable even at high temperature. Furthermore, the diffusion study of Pt_n clusters on g-C_3N_4 has shown that Pt_1 diffuses easily below the first layer of g-C_3N_4, but Pt_2 and Pt_3 are more stable on the surface due to stronger interactions with the support. We show the energy profiles at 873K, 1atm for the PDH mechanism over the Pt_n/g-C_3N_4 (n =1, 2, 3) catalysts. The single-atom Pt_1/g-C_3N_4 catalyst is the most favourable for adsorbing propane and propene but also for desorbing hydrogen. On Pt_2 and Pt_3 the activation of the second C-H bond and propene desorption are favoured.

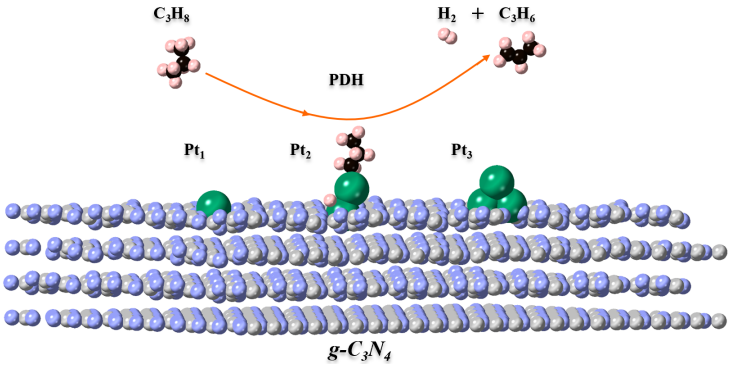

Figure 1. Pictorial representation of PDH catalysed by small Pt clusters anchored on g-C_3N_4.

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Unraveling the Oxidative Redispersion of Pt Nanoparticles Supported on Ceria via an Explorative DFT Study

Agustin Salcedo[1*], David Loffreda[1], and Carine Michel[1]

[1] *ENS Lyon, CNRS UMR 5182, Laboratoire de Chimie, 69364 Lyon, France.*
[*] *agustin.salcedo@ens-lyon.fr*

Keywords: water-gas shift, platinum, ceria, DFT

Introduction. Ceria-supported Pt is an active catalyst for the low-temperature water-gas shift (WGS) reaction employed in the production of pure H_2. However, it suffers from sintering problems, forming large nanoparticles (NPs) with low surface area.[1] The catalytic performance is strongly structure-sensitive, favoring small Pt NPs for CO oxidation.[2] Several strategies have been considered to minimize aggregation, including optimizing the Pt concentration and doping the support. Alternatively, the problem can be tackled by using the structural dynamics under operating conditions to tune the NP size. Oxidative treatments at ~500 °C promote nanoparticle redispersion and might prove useful to obtain optimal catalysts.[3] In this work, we propose a density functional theory (DFT) study to gain atomic-level insight into the redispersion of Pt NPs.

Computational details. DFT calculations were performed using the VASP code. We consider various stages of Pt redispersion namely (1) A NP of ~1.5 nm representing the sintered catalyst, modeled as a Pt_{147} cluster in its most stable high-symmetry homotope, a strongly-irregular truncated octahedron, (2) small 2–13 atoms Pt oxide clusters obtained via global optimization by a combination of genetic algorithms and sampling with a velocity rescaling thermostat, (3) single Pt atoms constituting the final state of the full redispersion. All Pt_xO_y systems were adsorbed on the CeO_2(111) surface.

Results and discussion. We find that single atoms are not accessible under the conditions of the oxidative treatment, since $\Delta G > 0$ for all the Pt_1O_y systems considered, indicating the treatment at 500 °C cannot redisperse Pt into single atoms. Instead, $Pt_{13}O_{12}$ species are found to be the most stable at 500 °C among the ones considered. This is in line with previous studies showing that Pt atoms are stabilized on CeO_2(111) by oxygen vacancies,[4] which are mostly unavailable under oxidizing conditions. Stable highly oxidized Pt single atoms are found at low temperatures, but the kinetics limit the redispersion under these conditions. At T > 800 K larger nanoparticles are preferred on CeO_2(111), although sufficiently large temperatures might induce a reconstruction of the support stabilizing single atoms.[5]

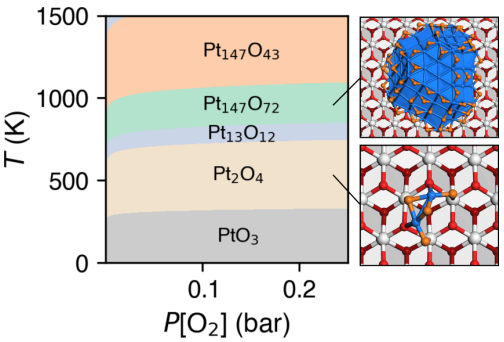

Figure 1. Ab initio thermodynamic map indicating the most stable species as a function of temperature and partial pressure of O_2.

Vibrational frequencies were also calculated to validate the cluster models by comparison with Raman spectra, identifying the main peaks associated with Pt–O and Pt–O–Ce bonds.

Overall, this study explores the stability of Pt_xO_y species supported on ceria and advances the understanding of the sintering and dispersion of Pt for catalytic applications.

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Selective oxidation of glucose with hydrogen peroxide: Structure sensitivity of the apparent activation energy

Ole Reinsdorf[1*], Camille Pellegrin[1,2], Christoph Schmidt[1], Matias Alvear[1], Kari Eränen[1], Dmitry Murzin[1],Tapio Salmi[1]

[1] *Åbo Akademi, Turku, Finland*
[2] *ENSICAEN, CAEN , France*
[*] *ole.reinsdorf@abo.fi*

Keywords: Structure Sensitivty, Gold Catalysis, Oxidation of Glucose

Introduction. The excellent biodegradable and biocompatable properties of aldonic acids have made them broadly applied in cosmetics, pharmaceuticals, food ingredients and detergents. They are classically produced by oxidation of glucose with molecular oxygen on noble metal catalysts, however hydrogen peroxide has been proven to exhibit excellent oxidant properties showing similar selectivities but with doubled reaction rates. The focus of previous studies has mainly been on reaction conditions and process intentisification. To illucidate the dependency on the catalyst properties and structure, a variety of catalysts with varying supports, metals and nanoparticle sizes were synthesised and tested in this work.

Experimental/methodology. The catalytic testing was performed in a 250 ml glass reactor fitted with a heating jacket and a teflon stirrer. The reaction was performed at low temperatures between 303-343K and ambient pressure with a starting concentrations of 0.2 M of glucose and 1.5M of hydrogen peroxide. Gold catalysts with varying nanoparticle sizes (2.5nm-38nm) and different supports were prepared. In addition, a series of catalysts with varying metals (Fe, Pd, W) were synthesised.

Among the metals, gold on alumina showed the best performance, however tungsten based has shown promising results as an alternative in the future. At a standard reaction temperature (343K), catalysts with higher nanoparticle size showed higher reaction rates while maintaining the same selectivity. The oxidation rate had a maximum around 6.5 and 7 nm, which is significantly higher than the classical rate-structure dependency observed for oxidations using oxygen on gold. However, at temperatures close to room temperature this dependency shifts its maximum to 2.5 nm. The determination of the apparent activation energy revealed an increase of the apparent activation energy with an increasing nanoparticle size with no significant change above 20 nm (Figure 1). The obtained apparent activation energy vs. particle size curves showed an excellent agreement with the theoretical model assuming differences in the adsorption energies on edges and terraces for a Langmuir-Hinshlewood-type reaction with first order for both reactants [1].

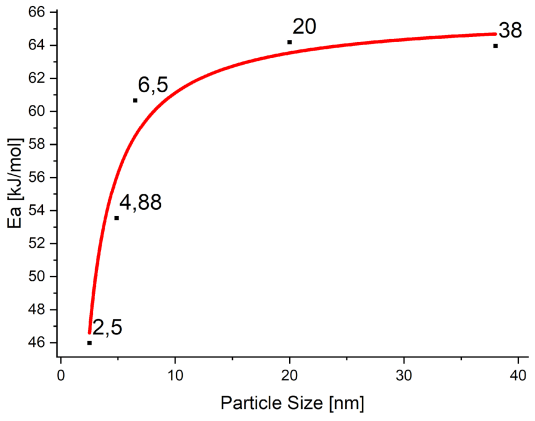

Figure 1. Fit of the theoretical model for the apparent activation energies for different gold cluster sizes.

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Acetonitrile as Novel Promoter for Palladium Supported Catalysts in the Direct Hydrogen Peroxide Synthesis

F. Sandri[1,2*], A. Lopez[1,3], F. Sedona[1], C. Schmidt[2], K. Eränen[2], M. Zecca[1], T. Salmi[2], C. Meneghini[3], P. Centomo[1]

[1]*Dipartimento di Scienze Chimiche, Università degli Studi di Padova, via Marzolo 1-I35131 Padova, Italy*
[2]*Johan Gadolin Process Chemistry Centre (PCC), Åbo Akademi University, Turku/Åbo, FI-20500, Finland*
[3]*Dipartimento di Scienze, Universita di Roma Tre, I-00146 Roma, Italy*
[*]*francesco.sandri.4@studenti.unipd.it*

Introduction. The direct synthesis (DS) of hydrogen peroxide (HP) is a hot topic in heterogeneous catalysis, as it represents a sustainable approach to produce this green oxidant for chemical industries.[1] The DS, catalyzed by supported Pd nanoparticles, suffers from the issue of selectivity, because water is the favored product and this is an obstacle for technological application. Well-established selectivity enhancers are chloride or bromide ions, but their application in industrial scale is prevented by corrosion problems.[2] A well-known feature of inorganic halides is their ligand properties towards Pd(II) to form palladium complexes, a feature which is shared with some common coordinating organic solvents. Starting from this, this work presents the use of a coordinating solvent as novel corrosion-free promoter for the DS reaction, thanks to their coordination properties.

Experimental/methodology. Pd catalysts supported on an ion-exchange resin based on a novel mesoporous polymer (Ps/SpDVB) [3] were investigated in the DS, both with a semi-batch reactor (SBR) and a trickle bed reactor (TBR). Further zeolite supported catalysts were investigated, together with commercial Pd on carbon as benchmark. The effect of acetonitrile (ACN) as coordinating solvent was studied by using a 10% vol ACN solution in methanol as the reaction mixture. The promotion effect of ACN is proposed by comparing DS experiments and characterization of fresh and spent catalysts, mainly with XPS, TEM and XAS.

Results and discussion. The results of the DS experiments with SBR setup are showing a selectivity enhancement as well as an increase in the production of HP when ACN is present in the reaction mixture (Figure 1). This effect is obtained only when the catalyst is supported on ion-exchange materials. In this case, the reconstruction of the metal phase occurs under reaction conditions, according to the formation of smaller Pd nanoparticles when compared to the fresh catalyst. Moreover, XPS and XAS show an increase of the Pd(II)/Pd(0) ratio after the catalytic experiment. This is further enhanced by the presence of ACN, together with the modification of the structural properties of the metal nanoparticles. This suggests a *release-and-capture* mechanism of the active metal, which starts from the formation of $[Pd(ACN)_4]^{2+}$ complexes that are then grafted to the support by ion-exchange. Their later reduced to form metal Pd nanoparticles; with this mechanism Pd species that are more active towards the DS are formed. By comparing the results with SBR and TBR setups, it is clearly seen that this mechanism and therefore the promotion effect depends on the reaction conditions used in the catalytic experiments.

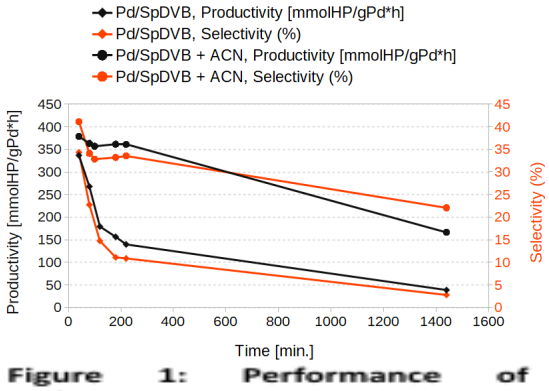

Figure 1: Performance of Pd/SpDVB in pure methanol (squares) and methanol:ACN 9:1 (circles).

Acknowledgments

We are grateful to Dr. Marcello Marelli (CNR Institute of Molecular Science & Technology, Milan) for TEM analysis. This project is financed by University of Padova, BIRD project PDiSC#03BIRD2020-UNIPD.

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Methylcyclohexane catalytic cracking over Y zeolite. A computational study

Astrid Sanchez[1*], Juan F. Espinal[2], Susana Ramirez[1]

[1]*Universidad Nacional de Colombia, Medellín, Colombia.*
[2]*Universidad de Antioquia, Medellín, Colombia.*
[*]*aesanchezp@unal.edu.co*

Keywords: Y zeolite, fluidized catalytic cracking, H^+ transfer.

Introduction. Different approximations to determine the kinetic of reactions involved in fluidized catalytic cracking have been developed. Given the high complexity of this process, model compounds representing the real mixtures are selected. Results for experimental catalytic cracking of methylcyclohexane (MCH) have been reported in several papers due to its importance in the formation of aromatic compounds. However, detailed mechanism, and thus chemical kinetics for the specific reaction, is not well understood. This study describes the catalytic cracking for MCH over Y zeolite based on electronic structure simulations, considering different important steps such as: adsorption, H^+ transfer from zeolite's active site to hydrocarbon and C-C bond cleavage, both for the ring opening and for the cracking reaction.

Methodology. MCH catalytic cracking reaction was evaluated employing *Gaussian 09* software [1]. Initially, isolated MCH and possible product molecules were fully optimized in their electronic ground state multiplicity using the density functional theory [2,3] with the hybrid functional B3LYP [4] and the 6-31G basis set. These calculations were followed by the evaluation of the adsorbed molecules on a cluster model of the Y-zeolite, which consists of 260 atoms, while the unit cell contains 576 atoms. All silicon atoms in the zeolite cluster have tetrahedral environments and one silicon atom, located in the zeolite cage, was replaced by an Al atom, which generates a Brønsted acid site. Interactions between the zeolite model and intermediate molecules were optimized employing the ONIOM method [5].

Results and discussion. Only unimolecular cracking reaction was considered, since hydrocracking, isomerization, coking, or any other secondary reaction are not considered. Isobutylene formation is shown as an example (Figure 1 left), since it has been reported as a product of cracking reaction [6]. A possible transition state for H^+ transfer from zeolite active site to MCH giving rise to the carbocation formation and subsequent C-C bond cleavage can be seen at the right side of Figure 1.

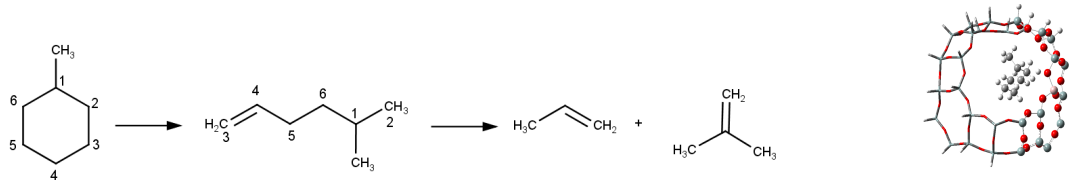

Figure 1. Left: MCH cracking reaction to produce propene and isobutylene ΔG_{800} = - 32.5 kcal/mol. Right: Activated complex for H^+ transfer from zeolite active site to MCH. ΔG^*_{800} = 37.4 kcal/mol.

Thermodynamics and detailed properties are obtained for reactant adsorption, olefin formation, as well as isobutylene and propene formation through cracking reaction, and finally desorption products allowing to propose a reaction mechanism in good agreement to the experimental reported results.

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Development of microowave reactors for high temperature catalytic reaction

Mirko Scanferla[a,b], Pierdomenico Biasi [c], Paolo Canu[a,b]

[a] *University of Padua, Industrial Eng. Dept., Padua, Italy.* [b]*K-INN Tech s.r.l., Padua, Italy,* [c]*CASALE SA, Lugano Switzerland.* [*]*Corresponding Author's E-mail address: mirko.scanferla@unipd.it*

Keywords: Microwave-assisted catalysis, Electrification of chemical engineering,

Introduction. Microwave-assisted catalysis holds great promise for enhancing sustainable industrial processes [1].By leveraging efficient energy transfer and localized heating, microwave heating can improve conversion and selectivity [2]. However, challenges related to catalytic materials, reaction kinetics, heating mechanisms, microwave emission, and scalability need to be addressed [3]. Overcoming these hurdles through further research will unlock the full potential of microwave-assisted catalysis, revolutionizing industrial processes for a greener future

Experimental/methodology. The magnetron power output control was modified to keep the desired temperature in the catalytic bed. Given the significant temperatures attained and the inherent challenge of point measurements within the catalytic bed, thermal homogeneity verification in the challenging catalytic bed involved grounded K-type thermocouples. An extensive experimental campaign included distributed thermal measurements using a quartz reactor (20 mm ID) with a Ni-based catalyst for methane reforming, mixed with SiC particles. Local thermal gradients were investigated in inert and reaction conditions. Microwave heating effectiveness was examined under transient and stationary regimes. A comparative analysis of energy balance between microwave and resistive heating highlighted the potential for innovative energy sources to replace conventional methods.

Results and discussion. Experimental campaign demonstrated the presence of resonance nodes in the cavity and reactor resulted in significant temperature gradients. Methane Dry Reforming reaction was studied. **Figure 1** showed that despite the temperature gradients, the catalyst's performance in terms of reactant conversion remained comparable to conventional heating methods. Both microwave and conventional heating achieved exceptional performance within the required temperature range (T > 900°C), with CO_2 and CH_4 conversions exceeding 95%. This indicates that microwave heating can effectively support the endothermic reaction and reduce reliance on fossil fuels. However, further investigation is needed to optimize the reactor design and improve selectivity due to the significant temperature variation across the reactor.

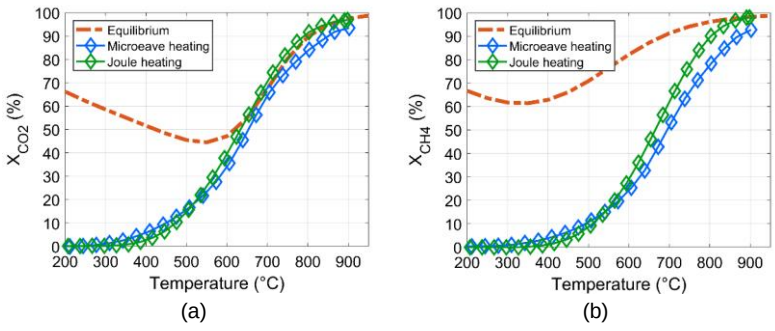

Figure 1: Comparison between microwave oven and conventional oven: (a) CO_2 conversion and (b) CH_4 conversion as function of controlling temperature

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Assessing the Role of Oxygen Vacancies for N_2O Decomposition over $CaMn_{1-x}Fe_xO_{3-\delta}$ Perovskites

Ana Serrano-Lotina[1], Emanuela Mastronardo[2], Pedro Ávila[1], Ignacio J. Villar-García[3], Laura Molina Nogal[1], Alicia Bayón[1], Sossina Haile[4], Juan M. Coronado[1*]

[1]*Instituto de Catálisis y Petroleoquímica. CSIC. 28049 Madrid, Spain*
[2]*Engineering Department, University of Messina. C.da di Dio, 98126. Messina, Italy.*
[3] CLAESS Beamline, ALBA Synchrotron, Carrer de la Llum 2-26, Cerdanyola del Valles, 08290, Spain.
[3]*Materials Science and Engineering, Northwestern University, Cook Hall, 60208 Evanston, IL, USA*
[*]*Corresponding Author':jm.coronado@csic.es)*

Introduction.

Catalysts based on redox oxides of transition or rare earth metals are very relevant in multiple processes such as pollutant elimination due to their capacity of oxygen exchange. Among them, perovskites, which are mixed oxides with general formula ABO_3, are very promising because of their high thermal stability, chemical versatility, and redox capacity. In these materials, position A of the structure is occupied by a large cation, generally of a rare or alkaline-earth element, while in the B-site hosts a cation of a transition-metal element with redox capacity, which mainly determines the catalytic performance. However, since the synthesis of perovskites requires high temperature, perovskites usually present very low surface area (<10 $m^2.g^{-1}$) and this can limit their catalytic efficiency.

Catalytic decomposition of N_2O into harmless N_2 and O_2 is a very suitable technology for controlling this powerful greenhouse gas released by industrial sources. Besides, this process is very suitable to explore the role of oxygen vacancies in catalytic processes because it does not yield any secondary product. Accordingly, in this work, we have tested for first time the catalytic activity of several $CaMn_{1-x}Fe_xO_{3-\delta}$ perovskites (x= 0.1 and 0.3) for the decomposition of N_2O in inert gas streams. These materials were selected for this study because thermodynamics of the oxygen vacancies formation have been experimentally determined in great detail, turning them ideal systems for thoroughly investigating the role of these defects on the catalytic removal of N_2O.

Experimental/methodology.

The catalytic activity of $CaMn_{1-x}Fe_xO_{3-\delta}$ perovskites (x= 0.1 and 0.3) for the decomposition of N_2O (1000 ppm_v) in an Ar stream (GHSV=50330 h^{-1}) was assayed at temperatures in the 350-850 °C range. Catalysts were characterized by XRD, and Raman spectroscopy, while Near Ambient Pressure (NAP) XPS was used to monitor redox processes on the surface.

Results and discussion.

For these catalysts, the temperature of 50 % conversion of N_2O was around 745 °C, independently of the Fe content. These values are comparable to those previously reported for other Mn and Fe perovskites under similar operation conditions. However, the activity of those materials declines moderately with time on stream. Thus, for $CaMn_{0.9}Fe_{0.1}O_{3-\delta}$ conversion of N_2O decreases from 55 % to 46% after 18 hours at 745 °C. Interestingly, an excess of oxygen release with regards to the expected considering only the N_2O decomposition stoichiometry was detected initially during the temperature rise. This reveals that the stoichiometry of the perovskite quickly changes in response to the increment of temperature, liberating oxygen. Since this process occurs simultaneously to N_2O decomposition, formation of N_2 was also observed but as expected, time evolution of this molecule does not show the maximum detected in the case of oxygen. Variation in δ of the perovskite and, accordingly, the evolution of O_2 concentration in the gas phase are entirely reversible with respect to the temperature in the presence of N_2O. This behavior suggests the existence of two independent routes leading to the release of oxygen in this perovskite. Thus, the thermodynamic mechanisms control non-stoichiometry of the solid by capturing/liberating O_2 from the surrounding atmosphere in response to the changes in temperature and oxygen partial pressure. This process has been further investigated by NAP-XPS. Simultaneously, some surface vacancies can assist to the rupture of the N-O bond of N_2O, as a part of a concurrent regenerative catalytic cycle yielding N_2 and O_2.

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Pd nanoclusters confined in functionalised metal-organic frameworks: selective, active and stable catalysts for hydrogenation reactions

Donato Decarolis[1], James King[2], Linda Zhang[3], Jeffrey Armstrong[4], Michael Hirscher[3], Andrew Beale[5], Alin-Marin Elena[6], Simone Meloni[7], Petra Ágota Szilágyi[8*]

[1]Cardiff University, UK, [2]Queen Mary University of London, UK; [3]Max Planck Institute, Germany; [4]ISIS Neutron and Muon Source, UK; [5]University College London, UK; [6]Daresbury Laboratory, STFC, UK; [7]University of Ferrara, Italy, [8]University of Oslo, Norway

p.a.szilagyi@kjemi.uio.no

Keywords: #1 MOFs, #2 selective hydrogenation, #3 hydride formation, #4 *operando* spectroscopy

Introduction. Metal-organic frameworks (MOFs) are a unique class of materials in terms of the tuneability of their pore geometry, chemistry, and flexibility, which makes them desirable from fundamental and application viewpoints. Furthermore, the size regime of the typical MOF pores (*ca.* 0.5-3 nm) coincides with size ranges in which other interesting physical phenomena take place. An example of such a phenomenon is the formation of interstitial hydride in Pd.[1] This is of relevance as Pd is a prolific catalyst for hydrogenation reactions but the phase activity and selectivity, *i.e.* whether the metallic (α) or the interstitial (β) phase is more active and/or more selective, has been subject of significant debate.[2]

With the help of the microporous non-flexible NH_2-UiO-66(Zr) framework we were able to nanoconfine Pd particles, as previously reported[3], in its pores and demonstrated that the so-obtained Pd nanoclusters cannot form the β-phase. We selected the butadiene hydrogenation reaction as model for the phase activity and selectivity test.

Experimental/methodology. We will discuss a combined theoretical-experimental approach, including structural optimisation and finite-size effects. Catalyts testing was carried out in a flow-reactor (H_2:C_2H_4:He=150:30:225) at ambient temperature, monitoring the exhaus stream using a GC-MS. The phase and chemical state of the Pd catalyst (which is *ca.* 1 nm, *i.e.* too small to diffract) was tested using a combintion of *operando* XAS, *in-situ* inelastic neutron scattering and, thermal desorption spectroscopy.

Results and discussion. Using the above approach, we demonstrate that the β-phase does not form.

Importantly, using this strategy, we were not only able to design a highly active, stable (Figure 1, and as shown through *operando* and *in-situ* characterisation), and selective catalyst but we were also able to relate this performance to the prevalence of the α-phase. In fact, we were able to produce fundamental insight into the ability of nanoconfined Pd nanoclusters to form hydrides or indeed absorb hydrogn in the first place. Our data, as opposed to previous suggestions[4], strongly suggests not only does the intersitial hydride phase not form on but even the absorption of sub-surface hydrogen (which is necessary for solid-solution formation) is unfavourable.

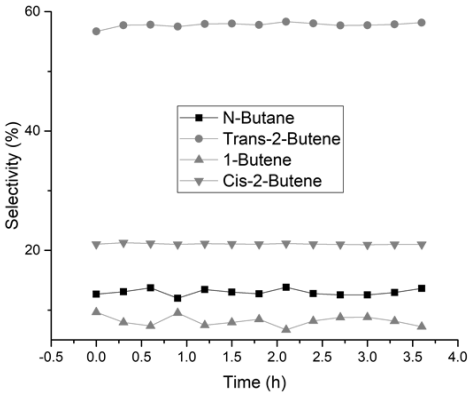

Figure SEQ Figure * ARABIC 1 Evolution of selectivity for 1,3-butadiene hydrogenation over Pd-laden NH_2-UiO-66 as a function of time on stream.

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Manipulation of the chemical reactivity of surfaces with 3d metals: New perspective on spin degrees of freedom

Satadeep Bhattacharjee[1*], *Swetareakha Ram*[1] *and Seung-Cheol Lee*[1,2*]

[1]*Indo Korea Science and Technology Center, Bangalore*
[2]*Electronic Materials Research Center, KIST, Seoul 136-791, South Korea*
[*]*s.bhattacharjee@ikst.res.in*
[*]*leesc@kist.re.kr*

Keywords: Heterogeneous catalysis, magnetism

Introduction. Catalysts containing 3d transition metals have recently gained interest due to their inexpensive cost and abundance. Heavy and 3d transition metal alloys are utilized in electrochemical reactions like the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). Another advantage of using such materials is that they introduce a new parameter that may be exploited to control the chemical reactions: The spin moments of 3d transition metals. From the theoretical point of view in heterogeneous catalysis the trend of the chemical reactivity is often explained in terms of the so-called d-band center model. We propose a generalized d-band center model where the chemical reactivity of the majority and minority spin-band electrons are separately evaluated [1]. We demonstrate that to understand the catalytic properties of spin-polarized materials one has to consider the d-band center model reformulated by us. Oxygen-based electrochemical reactions are the most important processes for batteries, fuel cells, etc. In this work, we looked at the possibility if one can reduce the overpotential for the oxygen reduction reaction (ORR) by changing the orientation of the spin moments of the oxygen atoms by a magnetic field. We studied the paramagnetic oxygen atoms adsorbed on PdFe surfaces and showed that the oxygen reduction reaction can be controlled using magnetic fields, particularly the overpotential [2]. Finally, we discuss how the traditional adsorption energy scaling relationship fails in bimetallic magnetic surfaces [3], with surface magnetic moments serving as critical descriptors in understanding the negative slopes in adsorption energy scaling relationships [4].

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Size Effects in Transition Metal Catalyzed Ammonia Decomposition

Jihao Wang, Shilong Chen, Malte Behrens*

Institute of Inorganic Chemistry, Kiel University, Kiel, Germany
**mbehrens@ac.uni-kiel.de*

Introduction.

Hydrogen economy provides a promising solution to the current global energy emergencies. However, the storage and transport of hydrogen from renewable energies is one of the major challenges. Under such scenario, it is possible to store hydrogen into ammonia, which has a big advantage in its high energy density and fully-fledged transportant infrastructure world-wide. Most importantly, hydrogen production via ammonia decomposition is a carbon-free process. So far, the best performing catalysts for ammonia decomposition are Ru-based. Nickel- and cobalt-based catalysts have been widely reported as the most potential catalysts to replace expensive Ru for ammonia decomposition.[1] Size effect of metal catalyst plays an important role in heteroegenous catalysis.[2] So far, only the size effect of Ru catalysts on ammonia decomposition has been systematiclly studied.[3] This work aims at the investigation of the size effect for these two non-nobal metal catalysts and at providing insight for ammonia decomposition catalyst design.

Experimental/methodology.

Ni/MgO and Co/MgO catalysts with different metal loadings were synthesized by a computer-controlled co-precipitation of mixed $Mg_{1-x}M_x(OH)_2$ hydroixdes with M = Co, Ni. The M/MgO catalysts were obtained by calcination followed by reduction. Kinetic measurements were carried out in a flow reactor (3%NH_3/Ar) with Micro-GC for detection. Structural analysis of the catalysts was performed by XRD and STEM.

Results and discussion.

Pre-catalysts are the solid solution of $Mg_{1-x}Ni_xO$ or $Mg_{1-x}Co_xO$, obtaining from the calcination of the hydroxide precurors. After reduction of the pre-catalysts, the size of metal particles increased from highly dispersed clusters to around 9 nm with the metal loading increased from 1 to 20 at.% ($0.01 < x < 0.20$). For increasing Ni loading, the reaction rate increased from 1 at.%-Ni/MgO (10 $mmol_{H2}$ mol^{-1}_{Ni} s^{-1}) to 2 at.%-Ni/MgO (38 $mmol_{H2}$ mol^{-1}_{Ni} s^{-1}) and then stayed at a similar value until 20 at.%-Ni/MgO (Figure 1a). Co catalysts showed a different behavior and the reaction rate continuesly increased from 1 at.%-Co/MgO (11 $mmol_{H2}$ mol^{-1}_{Co} s^{-1}) to 20 at.%-Co/MgO (61 $mmol_{H2}$ mol^{-1}_{Co} s^{-1}) (Figure 1b). 1 at.%-Co/MgO showed a much higher activation energy of 127.4 kJ mol^{-1} compared to catalysts with higher loading (~90 kJ mol^{-1}) while 1-5 at.%-Ni/MgO catalysts showed a similar higher activation energy of ~95 kJ mol^{-1} compared to higher loadings (~85 kJ mol^{-1}). Ni/MgO catalysts show high activity already at loading > 1 at.%, i.e. in the small clusters / particles range, while Co/MgO catalysts exhibit higher potential in the large particles range with an activity increasing with the loading / size. The kinetic results indicate that Co catalyst showed a distinctly sensitive size effect on ammonia decomposition as compared to Ni catalyst. Further experiments of NH_3-TPD for the nitrogen adsorption strength and H2-pulse-chemisorption for characterization of tiny metal particles are under way.

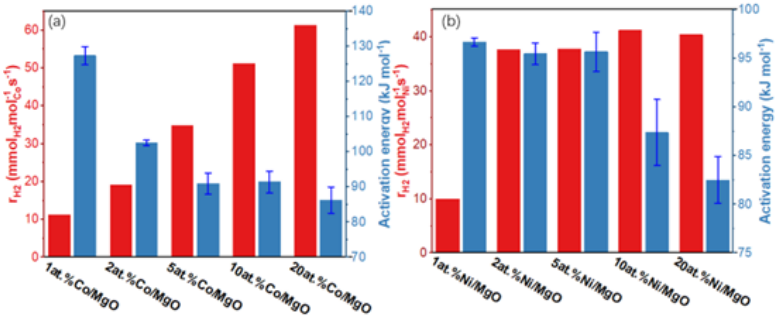

Figure 1. Reaction rate of H_2 production during ammonia decomposition at 500 C of and the corresponding activation energy for Ni and Co catalysts with various metal loading.

Reactions of Organic Molecules at the Water/Platinum interface: Parametrization of Density Functional Tight-Binding (DFTB)

Q. Wang[1,2], T. Niehaus[2*], S.N. Steinmann[1*]

[1]*Univ Lyon, ENS de Lyon, CNRS UMR 5182, Laboratoire de Chimie, F-69342 Lyon, France*
[2] *Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, Villeurbanne, France*
[*]*stephan.steinmann@ens-lyon.fr*; [*]*thomas.niehaus@univ-lyon1.fr*

Keywords: DFTB, water/platinum interface, repulsive potential parametrization, biomass conversion

Introduction. The water/metal interface is ubiquitous in heterogeneous catalysis and electrocatalysis, especially in the context of biomass conversion. Therefore, it is of great importance to obtain a detailed understanding of the this interface and the modification of the interaction of organic adsorbates in the presence of water compared to vacuum. Limited by the large size and complexity of the system, classical molecular dynamics (MD) and/or QM/MM simulations with force-fields models [1-2] are the conventional approaches for explicit water simulation. However, the many-body effects of water at the interface are neglected by force-fileds, as are surface reconstructions and modifications of adsorption modes in explicit water compared to implicit solvents. Herein, we parametrize Density Functional Tight Binding (DFTB), which can overcome these issues with a computational cost that is several orders of magnitude lower than DFT. We start by the water/platinum interface and then supplement the necessary parameters for Pt-C in order to describe the adsorption and reactivity of organic molecules at this archetypical interface.

Methodology. The parametrization of repulsive potential (E_{rep}) is critical for the transferability and overall accuracy of DFTB but is tedious. We start by establishing a relevant training and test set at the DFT level of theory and generate Pt-O and Pt-H E_{rep} parameters via the "DFTBparaopt" [3] and "CCS" [4] programs. These pair wise repulsive parameters are then augmented by many-body interactions as provided by the Chebyshev Interaction Model for Efficient Simulation (ChIMES) [5]. Finally, a large set of configurations are used to validate the method. This strategy is then applied to Pt-C and biomass molecules.

Results and discussion. The performance of different combinations of generated Pt-H and Pt-O E_{rep} parameter pairs were tested on a set containing ~4000 single-water/platinum-surface adsorption configurations that covers the diversity of water/platinum interaction. The best root mean square deviation (RMSD) of DFTB-calculated adsorption energies (E_{ads}) is 3.6 kcal/mol compared to DFT. The analysis shows that, compared to the DFT-calculated results, the DFTB predicted H_2O-Pt binding strengh is under-estimated on high-coordination surfaces like Pt(111) and Pt(100) while rather correctly reproduced on low-coordination surface atoms, e.g., addatoms. The ChIMES corrective potential is found to lower the RMSD to 1.76 kcal/mol and to increase the transferability between extended crystal surfaces and nanoparticles.

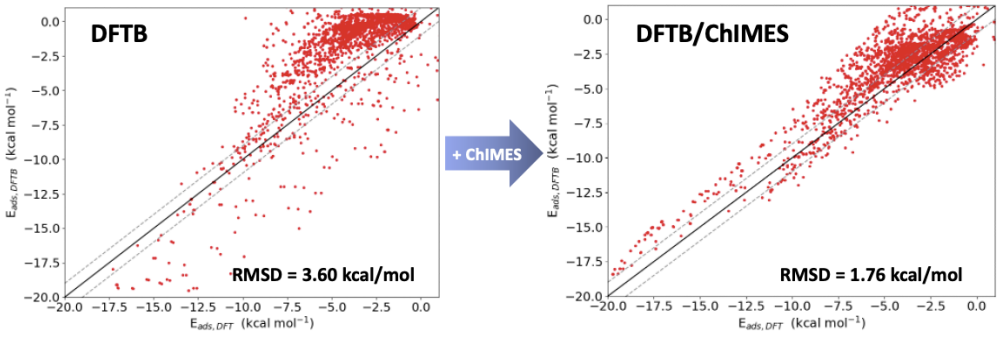

Figure 1: Parity plot of DFTB vs DFT adsorption energies of water on Pt surfaces, with/out and with ChIMES correction.

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Kinetics for the Dimerization of Ethylene to Butenes over the Ni-Al supported Silica based Catalysts

Jinsu Kim[1], Cheol-Woo Shin[1], Kwang-Eun Jeong[2], Chul-Ung Kim[2*], and Young-Seek Yoon[1**]

[1] *Graduate Institute of Ferrous & Energy Materials Technology(GIFT), Pohang University of Science and Technology(POSTECH), Pohang, South Korea*
[2] *Korea Research Institute of Chemical Technology(KRICT), Daejeon, South Korea*
[*] *E-mail: cukim@krict.re.kr*
[**] *E-mail: ysyoon@postech.ac.kr*

Keywords: Kinetics, Ethylene, Butens, Dimerization, Ni-Al supported Silica based Catalyst

Introduction.
Butenes constitute an important commodity which can be used as an intermediate in the production of a wide range of chemicals.[1] Typically, butenes are produced from naphtha steam cracking as a by-product. In other ways, the dimerization of ethylene to butenes(ETB) is an attractive possibility, exploiting the availability of ethylene via methathesis step.

The dimerization of ethylene to butenes over Ni-Al supported ordered mesoporous silica SBA-15 catalysts with different morphologies have been investigated compared to the activities of the other catalysts in our previous study, but also faced severe deactivation with time on stream.[2]

In this study, a kinetic study inculding deactivation is discussed for ETB reaction over the Ni-Al supported silica based catalysts based on the molecular based lumped kinetic model.

Experimental/methodology.
The ethylene dimerization was performed in a fixed-bed reactor (i.d. 6 mm) using 0.25 g catalyst at the pressure of 2 to 20 bar and the temperature of 200 to 380 °C. Ethylene was supplied at the rate of 2 to 8 ml/min with N_2 as a carrier gas. The experimental data after reacting for 1.3 and 10 hours, respectively, were used due to fast deactivation of the catalysts.
The kinetic parameters were estimated using experimental data by use of a genetic algorithm and ODE15s solver offered by Matlab R2023a.

Results and discussion.
Ni-Al suppoorted mesoporous silica based catalysts were good catalysts for ethylene dimerization, but are still faced severe deactivation with time on stream.

The conversion of ethylene was increased with increasing of the space time, reaction temperature, and reaction pressure at the early stage of the reaction (1.3 hour with time on stream). The major products at the this time were as followes such as 1-butenes > butane > ethane ≒ propylene ≒ hexene, whereas the major products after 10 hour were changed such as 1-butenes > hexene > butane due to the drastic declines of ethane and proplyene.

From the expimental results, apparent activation energies of ethylene conversion were estimated 1.7 and 37.5 kJ mol^{-1} at 1.3 and 10 hour, respectively.

Acknowledgments
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Iron impregnation on activated carbon for enhancing removal of humic acid in water

J.H. Kweon[1*], S.K. Ahn[1,2], W.J. Song[1,3]

[1]*Department of Environmental Enginneering, Konkuk University, Seoul, Korea*
[2]*Saman Corporation, Gyeongi-do, Korea*
[2]*Industrial technology research institute, Konkuk University, Seoul, Korea*
[*]*jhkweon@konkuk.ac.kr*

Keywords: Activated carbon, adsorption, impregnation, catalytic modification

Introduction

Humic acid (HA) is a naturally occurring complex organic matter and plays a key role in water and wastewater treatment (Lipczynska-Kochany, 2018). HA reacts with chlorine and produces carcinogenic by-products like tri-halomethanes and haloacetic acids during disinfection processes in water treatment plants (Park et al., 2019). Various removal technology has been considered and adsorption by activated carbon (AC) is recognized as a feasible option. However, adsorption capacities of HA should be enhanced to expand its application. Catalytic reaction of iron impregnation on surfaces of AC has been investigated to improve adsorption capacities of HA. Two different raw materials, i.e., coal- and coconut- based AC were utilized.

Experimental/methodology. The original granular AC was purchased from Calgon Carbon Corp. (USA) for the coal-based AC and from Samchully (Korea) for the coconut-based AC. Surface modification for iron impregnation was performed by an ion-exchange technique and treated by heat in a tube furnace with a temperature of 900 ℃ at a rate of 5 ·min-1 for 1 h under helium gas flow. Surface characterization was conducted with field emission scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), energy dispersive spectrometer (EDS), and zeta potential analysis. Isotherm experiments were also implemented to understand the adsorption properties.

Results and discussion. The surface modification increased iron contents of AC, which verified by EDS mapping images and XPS spectra analyses. The results of ion-exchange with different iron concentrations showed the increasing mean pore diameter and the decreasing specific surface area with increasing iron contents from 0.2 M to 2.0 M. The specific surface area was recovered by heat treatment and obtained approximately 5%~10% increases, which yielded the area almost similar to the original AC. However, the heat treatment decreased iron contents on the AC surfaces. Interplay between the catalytic component of iron and the active adsorptive sites were seemingly determined the adsorption capacities of humic acid. The isotherm equilibrium of humic acid showed that the maximum adsorption capacity was greater with high iron content AC than the original AC. The enhanced removal of HA was supported by the composition and spatial distribution of iron in the modified ACs. A reduction in the specific surface area and pore volume was observed with the modified AC. The increased adsorption capacity based on the accessible surface area revealed the importance of the catalytic surfaces of iron. The heat treatment largely recovered the pore structures and maintained a high adsorption capacity, which implied that particular strategies should be adopted to increase iron impregnated surfaces to improve HA removal.

Acknowledgments

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[2]*Saman Corporation, Gyeongi-do, Korea*
[2]*Industrial technology research institute, Konkuk University, Seoul, Korea*
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Mathematical Modeling of Response Dynamics of SnO_2-based Gas Sensors and Comparison with The Experiment

B. Atman[1], Y. Uludağ[2*], G. Karakaş[3*]

[1,2,3]*Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey*
[2*]*yuludag@metu.edu.tr*
[3*]*gkarakas@metu.edu.tr*

Introduction. The electronic properties of metal oxide semiconductors can easily be tuned by light, temperature, and chemical interactions with the environment. The latter makes them suitable for the gas sensor applications such as monitoring and detecting VOCs, toxic and hazardous gases such as CO, NO_x, etc. SnO_2 is the most frequently used and investigated material for gas sensor applications. The sensor response is based on the electrical resistance change due to the electron transfer between the semiconductor and the surface species. The reactions and electron transfer over the semiconductor surface are quite complex and have the primary importance on the sensor response characteristics such as response time, sensitivity, selectivity, etc. The response mechanism mainly relies on the ionized oxygen species (O^- and O^{2-}) over the surface and yet, the true nature behind the surface interactions with the oxygen species has not been adequately explained [1]. In this work, a comprehensive model is set-up to simulate the dynamic response of the thin film n-type SnO_2 gas sensor to CO in an air environment. For that reason, the ionization kinetics of oxygen over the surface, oxidation of CO and the mass transfer effects were incorporated into the mathematical model. The simulations were compared with the experimental results.

Experimental/methodology. The mathematical model consists of the diffusion of CO in 1D (through the thickness of the thin film), the oxygen adsorption and ionization over the surface, the reaction of CO with the ionized oxygen, electron transport between the adjacent grains and the electrical current transfer in 2D. The transient 2D simulations were performed by using the commercially available software COMSOL 6.0. The SnO_2 thin films were deposited on a glass substrate by using the sol-gel drop coating method. Under continuous dry air flow, DC resistance measurements of the sensor were obtained by using the digital multimeter GW Instek GDM-8255A. The gas sensor response was obtained with respect to step impulse of CO in air by using two six-port valves. The desired flow rates were adjusted by mass flow controllers.

Results and discussion. The effects of the temperature and film thickness on the dynamics of the sensor response were analyzed by simulations. The simulations were in good agreement with the experiments in terms of the response/recovery dynamics of the SnO_2 gas sensor having 7 µm film thickness to three different step changes in CO concentration in air (Figure 1). The increase in temperature results in an increase in O^- and total ionized oxygen density, while a decrease in O^{2-} density. Although faster response and recovery were obtained at high temperatures, response magnitude decreases with increasing temperature due to the faster replenishment rate of ionized oxygen species over the surface. The mass transfer limitations significantly decrease the sensor responses. In thick films, the current mainly flows near the external surface of the thin film as a consequence of the mass transfer limitations.

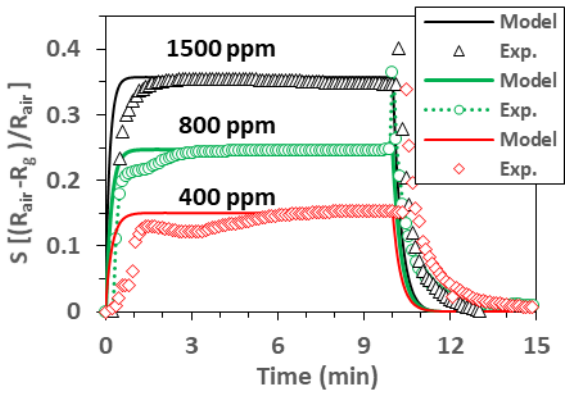

Figure 1. Comparison between experimental and simulation results in terms of the response of SnO_2 sensor having 7µm film thickness at T=528K.

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Refining and petrochemistry

Propylene production by butene cracking. Descriptors for ZSM-5-based catalysts

Pablo del Campo[1*], M. Teresa Navarro[1], Sohel K. Shaikh[2], Munir D. Khokhar[2], Furqan Aljumah[2], Cristina Martínez[1], Avelino Corma[1]

[1]*Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Avda. los Naranjos s/n, 46022 Valencia, Spain.*
[2]*Research & Development Center, Saudi Aramco, Dhahran-31311, Kingdom of Saudi Arabia*
[*]*pabdecam@itq.upv.es*

Introduction. The beneficial use of zeolites as shape-selective catalysts in petrochemical and refinery processes has been widely demonstrated. In order to maximize the catalytic activity and selectivity and to minimize catalyst decay, it becomes crucial to control the pore diameter (intrinsic zeolite pore dimensions and shape), the zeolite's chemical composition (Si/Al ratio, acid site density) and crystallite size (pore length), which determine the number and distribution of the active sites as well as the diffusion pattern. Besides the well-documented effect of the crystallite size and acid site density, there is another variable that may influence reactivity and diffusion in zeolites with different pores running along different crystallographic dimensions, such as ZSM-5, which is related to the morphology of the crystallites.[1] The high propylene demand drives researchers and industrial companies to the search for easy, inexpensive on-purpose technologies for its production. When propylene is obtained by FCC, butenes are also produced, so the direct conversion of butenes to propene is of high interest. In this work, this is approached by means of an oligomerization-cracking process, where the main challenges are minimizing the formation of aromatics and paraffins, not only because of selectivity issues, but also because of catalyst life. Therefore, we have studied and controlled the zeolite variables that result inpropene yield maximization during the catalytic cracking of butenes in the presence of ZSM-5 catalyst.[2]

Experimental/methodology. On the one hand, ZSM-5 zeolites with Si/Al 400 were synthesized with different crystallite sizes and morphologies. On the other, ZSM-5 zeolites with small crystal size and a square morphology were prepared with Si/Al ratios in the range of 200-600. Butene cracking experiments were performed under continuous fixed-bed conditions at 550ºC, atmospheric pressure and 1-butene concentration in the feed of 0.16 vol.%.[2]

Results and discussion. Chemical composition, crystal size and crystal morphology were defined as the descriptors that should control activity, selectivity and catalyst life. Thus, ZSM-5 zeolites were synthesized so that these descriptors were varied one at the time while maintaining the rest of the catalyst features constant, allowing us to rationalize the relative impact of each descriptor and their interplay. We found that square-shaped crystals with sub-micron sizes and Si/Al~300 (Figure 1a) facilitate propylene diffusion and decrease the extension of consecutive reactions by shortening the length of both sinusoidal and straight channels. The number of channel intersections is also reduced and, as a result, the formation of aromatics and branched oligomers leading to coke precursors was minimized, resulting in longer catalyst life. On the other hand, coffin-type ZSM-5 crystals show crystal discontinuities[3] and higher diffusional restrictions resulting in successive reactions leading to lower propylene selectivity and faster catalyst decay. Interestingly, both propylene selectivity and catalyst life were enhanced for large coffin-shaped crystals with intergrown particles (Figure 1b). We believe that this unexpected behavior is due to the preferential orientation of the twinned subunits, which expose preferentially sinusoidal pores (Figure 1c) and hence increase the proportion of openings giving access to the zig-zag channels for the whole crystal.[4] This allows more recracking events, but also prevents the formation and/or diffusion of large (poly)alkylated aromatic molecules, reported to be formed preferentially in the straight pores.[4] Moreover, light hydrocarbons, such as propene, will preferentially diffuse through the sinusoidal channels without being further converted into bulkier products,[5] while they will be consumed in consecutive reactions along the straight channels. Thus, in this case, the product shape selectivity is affected by the preferential exposure of the intergrowth facets giving access to the sinusoidal channels wherein the aromatics production is limited. Consequently and both propylene selectivity and catalyst life are enhanced, even for these large crystallites.

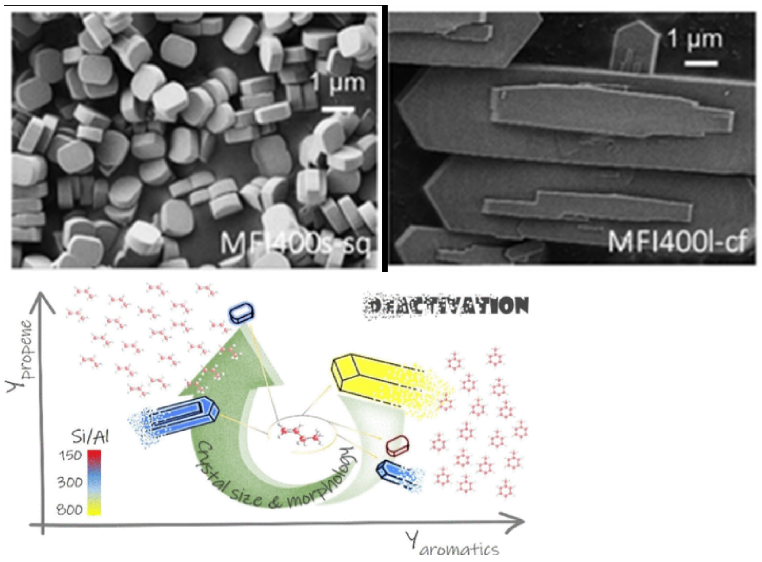

Figure 1. (a, b) FESEM micrographs of two differently synthesized ZSM-5 and (c) balance of diffusional (crystal size and morphology) and compositional (Si/Al ratio) effects for maximizing propylene production and catalyst life.

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The Role of Formaldehyde in the Methanol-to-Hydrocarbons Conversion

Vladimir Paunović[1,2*], Patrick Hemberger[2], Andras Bodi[2], and Jeroen A. van Bokhoven[1,2]
[1] *Institute for Chemical and Bioengineering, ETH Zurich, Zurich, Switzerland*
[2] *Paul Scherrer Institute, Villigen, Switzerland*
[*] *vladimir.paunovic@chem.ethz.ch*

Introduction. Formaldehyde (CH_2O) is an important intermediate that affects the performance of zeolite catalysts in the methanoltohydrocarbons (MTH) conversion.[1-3] This species, which is proposed to arise from Brønsted acid site (BAS)-catalyzed hydrogen transfer (HT) from methanol, readily transforms alkenes into dienes and methylated benzenes (MBs), thus favoring the products of the arene cycle.[1,2] Besides, CH_2O facilitates the conversion of MBs into polycyclic aromatic hydrocarbons, which are the main deactivating species.[2] However, the CH_2O reaction pathways and their dependence on the catalyst structure are still elusive, which is mainly caused by the challenging detection of this intermediate.

Experimental/methodology. The photoelectron photoion coincidence (PEPICO) spectroscopy combined with isotope labeling experiments and catalyst testing were used to investigate the formation and reactivity of CH_2O in quartz and stainless steel reactors, over bed diluents (silicon carbide and quartz), and ZSM-5 catalysts with low (15, Z_{15}) and medium (40, Z_{40}) Si/Al ratios.[3]

Results and discussion. The PEPICO experiments revealed that stainless steel reactor walls and silicon carbide diluent exhibit methanol-to-formaldehyde conversion activities that are higher or comparable to those of the zeolite catalysts under similar conditions (**Fig 1a**). Their activity stems from methanol dehydrogenation over transition metal sites, which yields hydrogen and carbon monoxide as byproducts. Thus produced CH_2O readily reacts in the MTH reaction, causing a decrease of the propenetoethene ratio and the reduction of the catalyst life-time (**Fig 1b**). Low activity of quartz enabled to study the CH_2O reactions over ZSM-5 catalysts (**Fig 1a,c**). At low conversions, methane is generated in stoichiometric amounts with CH_2O, which along with low yields of C_{2-4} alkenes and non-detectable formation of alkanes, arenes, and dienes implicates that HT between metoxy groups is the prevailing reaction in the first phase of the MTH conversion. This reaction displays the first order dependence with respect to methanol and moderate activation energy (ca. 80 kJ mol^{-1}). With increasing conversion, a decrease of CH_2O yield coincides with the evolution of dienes and MBs, indicating the involvement of CH_2O in their formation. This is corroborated by the CH_2O cofeeding, which led to immediate decrease of alkene, and increase in production of MBs and methylated naphthalenes (**Fig 1d**). Thereby, identification of fulvene suggests that it may be the central species mediating the CH_2O-induced transformation of alkenes to arenes. Notably, the yield of CH_2O shows faster decrease for less stable Z_{15} than for more stable Z_{40} catalyst (**Fig 1c**). These results provide a hint that lower activity of less acidic zeolites in the CH_2O-mediated reactions may be the central source of their lower coking propensity. Such relationships between the CH_2O activity and catalyst stability are tackled in our ongoing research.

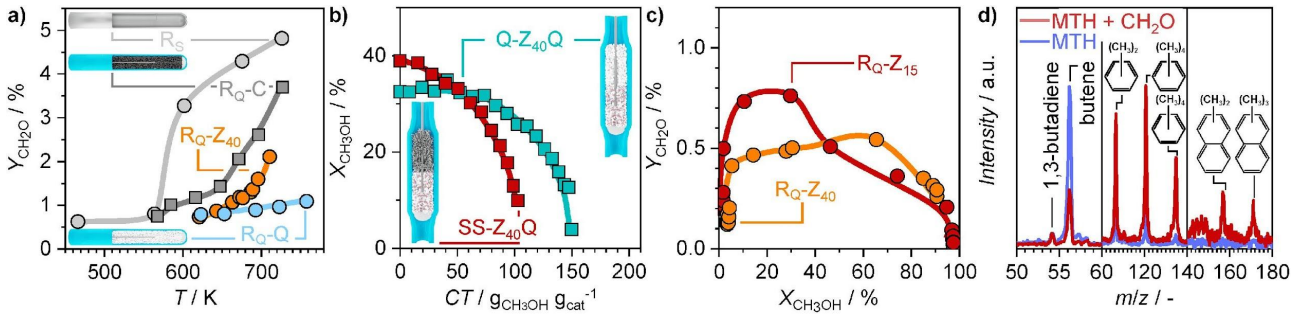

Fig. 1. a) CH_2O yield in stainless steal (Rs) and quartz reactors (R_Q) filled with SiC (C), quartz (Q) and Z_{40} zeolite. b) Conversion vs. cummulative turnover in the MTH reaction in the presence of steal and quartz. c) CH_2O yield vs. conversion over Z_{15} and Z_{40} zeolites. c) Change of product distribution in the MTH reaction upon CH_2O co-feeding.

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Application of Ga-based catalysts for the non-oxidative dehydrogenation of methanol to formaldehyde and hydrogen

M. Merko, S. Delsing, W. Busser, M. Muhler*

[1] *Ruhr-Universität Bochum, D-44780 Bochum, Germany*
**muhler@techem.rub.de*

Introduction. The non-oxidative dehydrogenation of methanol (CH_3OH) to formaldehyde (CH_2O) is an alternative to the classical oxidative dehydrogenation/partial oxidation applied in the industrial production of CH_2O. Its advantage is the production of anhydrous formaldehyde required for the synthesis of polyoxymethylene dimethyl ethers and H_2 as a coupled valuable product. In spite of intense reseach[1] an industrially relevant process has not been established yet. The promising catalytic performance of bulk β-Ga_2O_3[2] as well as an enhanced yield of CH_2O as a reaction intermediate over Ga/HZSM-5[3] were recently reported.

Experimental/methodology. Supported catalysts with varying Ga content were prepared by wet impregnation of fumed SiO_2 and γ-Al_2O_3 followed by calcination in air. The characterization of the materials included N_2 physisorption, ICP-MS, XRD, Raman spectroscopy, TEM/SEM-EDS, XPS, NH_3 TPD, DRIFTS, and TPO. The activity of the materials was tested in a home-made laboratory set-up using a fixed-bed reactor in the temperature range of 200-650 °C while applying a flow of 2.6-2.7% CH_3OH in 300 mL min^{-1} N_2.

Results and discussion. Figures 1a demonstrates that both the choice of the support material and of temperature had a significant impact on the product distribution. Formation of CH_2O was favored above 550 °C for 8 wt% Ga/SiO_2 with DME being a major byproduct at lower temperatures. The latter was due to the intrinsic activity of the support in case of γ-Al_2O_3 and possibly accompanied by the formation of new active sites upon interaction of gallia with the support for SiO_2. Additionally, variation of the Ga content and the support affected the deactivation rate (Fig. 1b) as well as the amount, composition and thermal stability of the carbon deposits formed at the catalyst surfaces. Deactivation was reversible for all catalysts, which was fully regenerated by a treatment with O_2. By applying reaction-regeneration cycles, prevention of rapid deactivation was achieved resulting in a stable performance of the catalysts (25 wt% Ga/SiO_2, Fig. 1c).

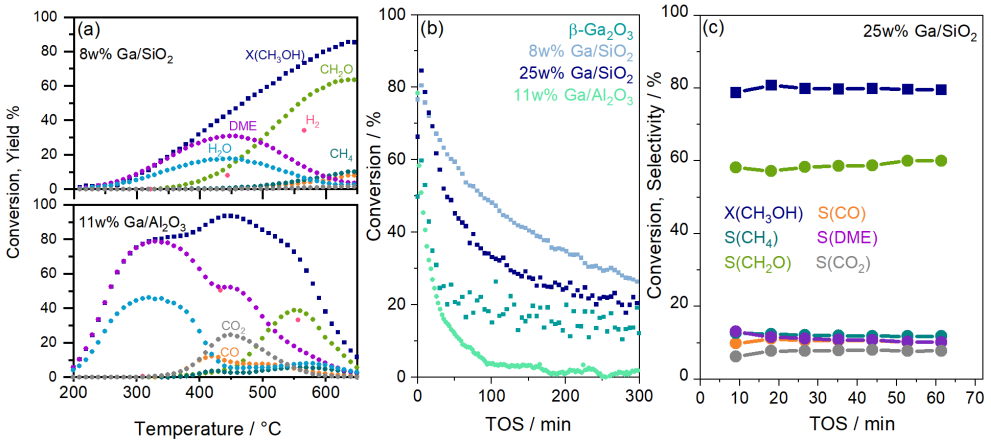

Figure 1. (a) Effect of temperature on the product distribution over 8 wt% Ga/SiO_2 and 11 wt% Ga/Al_2O_3; (b) change of conversion with TOS at 550 °C; (c) catalytic performance of 25 wt% Ga/SiO_2 at 550 °C obtained when periodic regeneration of the catalyst was performed using a ratio of reaction time to regeneration time of 2.7:1.

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Second-generation approaches for the production and distribution of green H_2

G. Centi* and S. Perathoner

The University of Messina and the European Research Institute of Catalysis aisbl, Messina/Italy and Brussels/Belgium
** E-mail: centi@unime.it*

Keywords: green H_2, photoelectrocatalysis, plasma-assisted methane decomposition, LOHC, e-SMR

Introduction. "Green" hydrogen will play a crucial role in the future of a carbon-neutral society, with multiple applications from carbon-intensive industries to transport, power and buildings sectors [1]. Thus, it is surprising that the discussion is focused almost only on electrolysis, an energy-intensive process. This lecture will discuss examples of alternative H_2 production and novel possibilities for hydrogen vectors to explore new opportunities in hydrogen production and distribution [2].

Discussion. The lecture will discuss some examples of alternatives to electrolysis in producing green and even carbon-negative hydrogen. After introducing why it is necessary to go beyond electrolysis-only technologies, and briefly discussing the production of H_2 from waste [3], the concepts of i) H_2 from electrified SMR (steam methane reforming) and ii) green H_2 produced in a plasma-assisted process from bioCH_4 are presented. Both are just-started projects (EreTech and MECCA, respectively).

For hydrogen distribution (H_2 vectors), the catalytic hydrogenation of LOHC (Liquid organic hydrogen carriers) coupled with lignin derivatives oxidation to reduce LOHC production costs and links biowaste valorisation (biorefinery) to H_2 economy is introduced. This is also a just-started EU project (EPOCH). The final example regards the possibility of a PEC (photoelectrocatalytic) device integrating the chemical storage to allow a continuous (24h) production of green H_2. It is the first example of developing artificial trees for continuous or on-demand production of green H_2 in a distributed mode.

These examples highlight thus the many possibilities beyond the too-limited panorama of studies in the green H_2 arena. There is a need to accelerate innovative directions in green area production and distribution to address the challenge of a carbon-neutral society more effectively [1,2]. Catalysis and chemical engineering play a crucial role in realising this challenge [5,6].

Acknowledgements
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Unexpected formation of aromatics from ethylene conversion on non-zeolitic Ni catalysts

*M. Armbruster, U. Bentrup, H. Atia, D. Linke and U. Rodemerck**
*Leibniz Institute of Catalysis, 18059 Rostock, Germany, *uwe.rodemerck@catalysis.de*

Introduction. Ni on silica-alumina prepared by grafting converts ethylene mainly to propene and butenes as already described in the literature [1,2] whereas over Ni/SiO_2 aromatic compounds are formed. Nickel was doped on silica and silica-alumina by three methods to obtain Ni^{2+} surface species with different vicinity and dispersion. The formation of aromatic compounds requires the interplay of metallic and acidic centres [3]. On the contrary to well-known metal-doped MFI zeolites, our new Ni-silica catalysts do not possess any Brønsted acidity which suggests a different reaction mechanism of aromatics formation.

Experimental/methodology. Commercial silica-alumina (Siral 70), SiO_2, MCM-41(MCM) and silicalite-1(S1) were used as supports for ca. 1-2 wt% Ni loading. The catalysts are prepared either by incipient wetness impregnation ($1Ni/SiO_2$_i, 1Ni/MCM_i), template-ion exchange (3Ni/MCM_t) or by grafting of $Ni(acac)_2$ (2Ni/MCM_g, $2Ni/SiO_2$_g, 1Ni/S1_g). Selected samples were characterized by various techniques and evaluated in ethylene conversion at atmospheric pressure and 375°C. The reaction was carried out in apparatus equipped with 15-parallel continuous flow fixed-bed reactors. The catalysts were screened consecutively, reactor by reactor. The products consisting of paraffins, isomers, olefins and aromatics were registered by gas chromatography. Ethylene conversion (X) and product selectivities (S_i) were calculated from the respective concentrations at inlet/outlet of reactor and for selectivity a coefficient equal to C-atoms in corresponding molecule was used. S_{coke} was calculated as difference to 1.

Results and discussion. All Ni-silica catalysts possessed amorphous structure and diverse mesopores, but FTIR spectra of CO adsorption differ considerably: Ni impregnated samples show no CO adsorption on Ni^{2+} surface species but only bands at 2157 and 2135 cm^{-1} connected with CO adsorbed on OH groups of silica. This agrees with the absence of acidic Lewis sites on these catalysts as measured by pyridine adsorption. $2Ni/SiO_2$_g and 2Ni/MCM_g, prepared on different Si-supports by grafting of $Ni(acac)_2$, displayed an additional band in the IR spectrum at 2178-2180 cm^{-1} that can be assigned to Ni^{2+} species bound through OH groups linked to Si. On 1Ni/S1_g two additional bands were observed and assigned to diverse Ni^{2+} species. XRD and TPR results confirmed as well that grafting method is much better suited to reach highly dispersed surface Ni^{2+} sites than impregnation. Preparation method affects the anchoring of Ni species on the support and finally the interplay of Ni-support active sites. Hence, the reaction pathway ends up in different product distribution. Aromatics were observed on all-silica catalysts made by Ni grafting, where the highest selectivity of 25% was achieved on 2Ni/MCM_g, Fig.1. Ni ion-exchanged sample has shown low selectivity to aromatics while on catalysts prepared by simple impregnation no aromatics were observed at all. IR spectra of adsorbed pyridine and carbon monoxide recorded for impregnated $1Ni/SiO_2$_i and 1Ni/MCM_i showed neither Lewis acidic sites nor adsorbed CO on surface Ni^{2+}species. The formation of aromatics from ethylene occurs over catalysts with Ni^{2+} surface species bound by O-bridges to silica. These sites do not involve any H^+-acidic sites. Such species have different electronic properties compared to those present in Ni/silica-alumina (Ni^{2+}-O-Al) as concluded from different wave number in IR spectrum of adsorbed CO (2180 *vs* 2195 cm^{-1}). The ability for aromatics formation and its selectivity depends on the kind of Ni species and its dispersion that can be controlled by the preparation method.

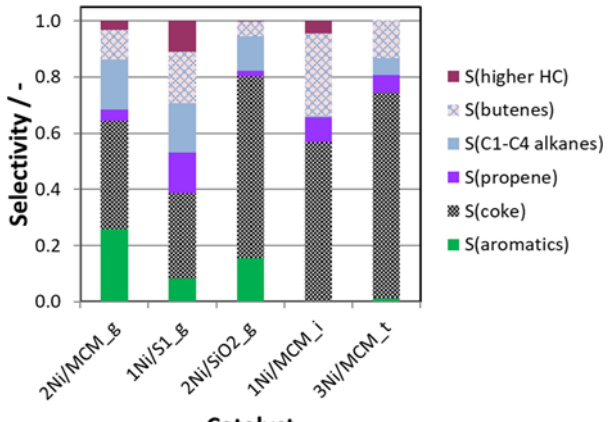

Fig 1. Product distribution at X(C_2H_4) of about 5%

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Methane dehydroaromatization over Mo/WO_3-ZrO_2 catalysts

Jhonattan D. Manosalvas Mora[1], A.K.M. Kazi Aurnob[1], Ashraful Abedin[1], James J. Spivey[1*]

[1] *Louisiana State University and Agricultural and Mechanical College, Baton Rouge (LA), USA*

** jjspivey@lsu.edu*

Introduction. Methane dehydroaromatization (MDA) is widely reaction studied by a bifunctional Mo/H-ZSM-5 catalyst, to produce benzene from methane in a single step ($6CH_4 \rightarrow C_6H_6 + 9H_2$; ΔG°=432.5 kJ/mol). This chemical reaction has been classified as one of the most complex problems of catalysis [1] because of thermodynamic limitations and carbonaceous depositions which preclude steady state conditions and promote rapid deactivation. Here, we demonstrate the use of a novel Mo/WO_3-ZrO_2 (Mo/W-Z) catalyst, its characterization, and elucidate its advantages and/or disadvantages compared to literature. The 1%(wt.) Mo/W-Z catalyst showed the best stability at 600°C during TOS = 1000 min.

Experimental/methodology. The synthesis process involved two stages [2]. First, synthesis of the support, and second, impregnation of molybdenum oxide on to the support. In short, certain amount of ammonium metatungstate was impregnated into zirconium (IV) hydroxide using the dry impregnation method. Next, the WO_3/ZrO_2 (W-Z) catalytic support was dried, calcinated, and impregnated with ammonium heptamolybdate tetrahydrate [3], producing three loadings of 1% (wt.) Mo, 3% (wt.) Mo, and 6% (wt.) Mo,. The fresh, spent, and carburized samples were characterized by XRD, XPS, TEM-EDX elemental mapping, SEM-EDX elemental mapping, BET, NH_3-TPD, pyridine DRIFTS, H-NMR, EXAFS, and XANES. The catalyst tests were carried out using a PID Eng & Tech 9.1mm Hastelloy X tubular reactor (Serial: MA 12212MICROMERITICS) with TOS = 1000 min. Products were quantified downstream with an on-line Shimadzu GC-2014 and identified using a Shimadzu GCMS-QP2010 system. The reactions were completed in two stages [4]. The first stage consists of Mo carburization. The second stage involves MDA with CH_4 as the only reactant at temperature ranges from 600°C to 800°C at constant 1.013 $bar_{(a)}$ and 1500 mL/g·h.

Results and discussion. The main products of the reaction at each temperature were ethylene, ethane, propylene, and benzene. However, other aromatic products of higher molecular weight were not identified nor quantified. Furthermore, in figures from 1a to 1c, the results of the catalytic runs showed that samples with 6%(wt.) Mo loading at 700°C and 650°C produced the highest amounts of benzene within the first 100 min, but after this period deactivation made benzene not detectable after 300 minutes (at 700°C) and 850 minutes (at 650°C). However, the sample with 1%(wt.) Mo loading at 600°C exhibited highest stability and slowest deactivation. In fact, 1%(wt.) Mo at 600 °C reaction generated approximately 17 times more benzene than 6%(wt.) Mo at 700 °C (TOS = 300min), and 14 times more benzene than 6%(wt.) Mo at 650 °C (TOS = 900min). Figure 1d shows that samples have Bronsted (B) and Lewis (L) acid sites. B sites are essential, among other things [5], in ethylene oligomerization. In addition, there is no significant change in transmittance intensity which could mean that B and L sites were not affected by Mo impregnation. Finally, XRD patterns of all the tested samples show tetragonal (T) and monoclinic (M) zirconia phases, and crystalline WO_3 (W).

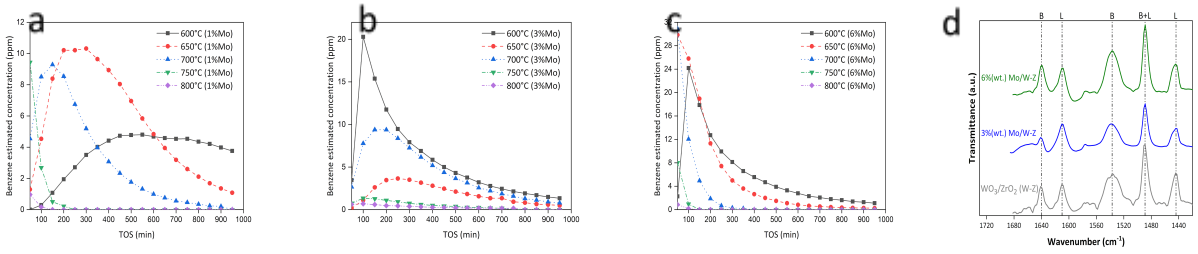

Figure 1. Benzene estimated concentration at different temperatures with a) 1% (wt.) Mo/W-Z, b) 3% (wt.) Mo/W-Z, c) 6% (wt.) Mo/W-Z, and d) Pyridine – DRIFTS at 100°C.

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Minimizing rare earth content of FCC catalysts: understanding the fundamentals on combined P-La stabilization

Cristina Martínez[1*], Alejandro Vidal-Moya[1], Bilge Yilmaz[2], CP Kelkar[2], Avelino Corma[1]

[1] *Instituto de Tecnología Química (UPV-CSIC), Universidad Politècnica de València-Consejo Superior de Investigaciones Científicas, Avda. de los Naranjos s/n, Valencia, 46022, Spain*
[2] *BASF Corporation, 25 Middlesex-Essex Turnpike Iselin, Iselin, 08830, United States*
[*] *cmsanche@itq.upv.es*

Keywords:

Catalytic cracking, zeolite USY, hydrothermal stabilization, phosphorus, rare earth

Introduction.

Fluidized Catalytic cracking (FCC), one of the main conversion processes in conventional refineries, employs a multicomponent catalyst with Y zeolite as the main source of activity and selectivity towards value added products.[1] In order to meet the severe requirements of the FCC unit, the hydrothermal stability of this large pore zeolite is traditionally improved by means of controlled hydrothermal treatment that could be coupled with acid washing cycles, by ion exchange with rare earth (RE) ions or by a combination of both.[2] Phosphorus has also been described as stabilization element, and although most of the studies are based on ZSM-5 zeolites, a new Y zeolite containing FCC catalyst based on the partial substitution of RE by P was developed, that allowed obtaining the same yield structure and activity as its conventional RE stabilized counterpart in vacuum gas oil (VGO) feed applications.[3]
Here, we present a systematic study where P- and La-free USYs with different dealumination degrees are compared with the corresponding USYs containing P or La alone or a combination of both.

Experimental/methodology.

Three ultrastable Y (USY) zeolites were prepared by pre-stabilization at different temperatures, 500, 600 and 700ºC (USY500, USY600 and USY700). La was introduced by ion exchange and P by wet impregnation. Comercial catalyst were tested for VGO cracking in a circulating riser unit. In-house prepared (P/La)-USYs were tested for VGO cracking in a MAT unit.

Results and discussion.

The results obtained confirmed that the properties of the starting USY zeolite carry a strong influence on the stabilization degree of elements such as P or La. Thus, for USYs obtained under milder pre-stabilization conditions, the presence of highly dispersed cationic EFAl species already exerts a stabilization function towards hydrothermal treatments at 750ºC. Only a strongly dealuminated USY such as USY700, does clearly benefit from the introduction of high REO loadings, thanks to the preservation of a larger amount of BAS. A similar trend was observed when adding P as single stabilization element, and only for the more dealuminated USY700, the addition of 1.0 wt% of P as H3PO4 or MAP resulted in a more active catalyst with similar liquid fuels and lower coke selectivity as compared to the reference P-free zeolite. However, it is possible to improve the catalytic behavior of a high UC size USY, with a low dealumination degree, to levels comparable to those given by a high REO La/USY by properly combining P and La as stabilization elements.

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The effect of the support pore structure on the oxidative desulphurization of dibenzothiophene

A. Nurwita*, M. Trejda

*Departement of Heterogeneous Catalysis, Faculty of Chemistry, Adam Mickiewicz Univerisity, Poznań, Poland, *ardnur@st.amu.edu.pl*

Introduction. Oxidative desulfurization (ODS) is one of the promising processes for desulfurization of fuels. Compared to conventional catalytic hydrodesulfurization, ODS can be carried out under mild reaction conditions and requires less energy. The success of the ODS process is determined by the catalyst efficiency in the oxidation, which strongly depends on the nature of the active centers and the type of support material. In this work two mesoporous silicas, i.e. SBA-15 and MCF, were applied as supports for Brønsted acid sites. The catalytic activities of the materials obtained were determined in oxidative desulphurization of the model compound, i.e. dibenzothiophene.

Experimental/methodology. SBA-15 and MCF supports were obtained by hydrothermal synthesis [1-2]. The organic template (Pluronic P123) was removed by calcination at 500°C. To generate Brønsted acidity, the supports were modified by 3-(trihydroxysilyl)-1-propanesulfonic acid (TPS) by grafting method keeping the Si/TPS molar ratio of 10 (in toluene at 100°C). The materials obtained were characterized by XRD, low temperature N_2 adsorption/desorption, elemental analysis and pyridine adsorption followed by FTIR measurements. Oxidative desulphurization of dibenzothiophene (DBT) was performed in EasyMax Workstation using H_2O_2 as an oxidant and different amounts of catalysts at various temperatures, H_2O_2/S ratios and reaction times.

Results and discussion. TPS containing catalysts based on SBA-15 and MCF were synthesized. Successful incorporation of TPS species on the surface of SBA-15 (0.70 mmol g^{-1}) and MCF (0.75 mmol g^{-1}) supports was confirmed by elemental analysis. The results were in agreement with the pyridine adsorption experiments combined with the FTIR spectroscopy. The results indicated that TPS/SBA-15 and TPS/MCF catalysts contained Brønsted acid sites (BAS). The concentration of BAS in MCF support was a little higher. The low-temperature N_2 adsorption/desorption experiments confirmed the mesoporous structure of the materials obtained. Incorporation of TPS species slightly decreased the surface area and pore diammeter, however, the samples maintained their mesoporous character. The catalytic tests performed with the participation of TPS/SBA-15 led to the aggregation of catalyst particles during the reaction, significantly limiting the activity in the ODS process (maximum 52% of conversion). On the other hand, TPS/MCF material appeared as an effective catalyst for ODS processes. Up to 99% DBT conversion was achieved at optimized reaction condition (Figure 1). Moreover, TPS/MCF maintained its catalytic activity over subsequent reaction cycles.

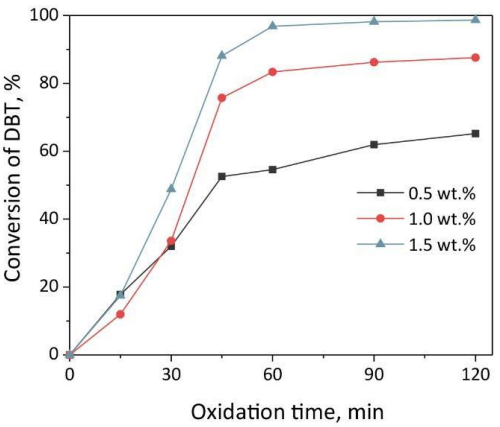

Figure 1. Catalytic activity of TPS/MCF (temp. 80°C; H_2O_2/S = 6:1, 1000 rpm)

Acknowledgments

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Investigation of induction period and oxygen species of chromium oxide catalyst for fluidized dehydrogenation of propane

H. Park, W.C. Choi, Y.K. Park, D.S. Park*

Korea Research Institute of Chemical Technology, Daejeon, South Korea
**dpark@krict.re.kr*

Keywords: Propane dehydrogenation (PDH), Chromium oxide, Induction period, Circulation fluidized bed

Introduction. The fluidized bed dehydrogenation has excellent advantages in terms of energy efficiency and low emissions of NO_x and CO_2. However, it is challenging to develop a catalyst with high activity and propylene selectivity within a short residence time. Formation of propylene is delayed during a few seconds due to the formation of CH_4, CO and CO_2 over commercial Pt or Cr catalysts. To better understand this induction period, we figured out correlation between the initial selectivity to propylene and the formation of oxygen species on a chromium-alumina catalyst. We also introduce a catalyst-development strategy for fluidization process that reduces the induction period by control of oxygen species on catalyst and increases propylene selectivity within 3 s of the commencement of the reaction.

Experimental/methodology. The products were collected and analyzed on the second timescale reaction system. Analytical method (TPO) was carried out for distinguishing different oxygen species that develop over the Cr/Al_2O_3. A detailed correlation between the initial selectivity to propylene and the formation of oxygen species on a chromium-alumina catalyst was established by O_2-TPO and Raman analysis.

Results and discussion. Catalytic behavior at a very beginning of the reaction was related to diffrent oxygen species over the Cr/Al_2O_3 catalyst. Selective oxygen species in chromium oxide were rarely reduced or oxidized by H_2-TPR and O_2-TPO. Otherwise, non-selective oxygen species that are easily reduced of oxidized, were confirmed not highly dispersed, but are accumulated on the surface of the catalyst by the Raman analysis. The production of CO_x in the early stage of the reaction was mainly caused by weakly bonded oxygen species on the surface of the catalyst, which favor the deep oxidation of propane. Furthermore, we suggest strategies to design catalyst for fast fluidized PDH process. One is increasing the amount of selective oxygen species by calcination method and the other is to selectively reducing non-selective oxygen species by pre-reduction with reductive gases which is applicable to fast-fluidized bed PDH process.

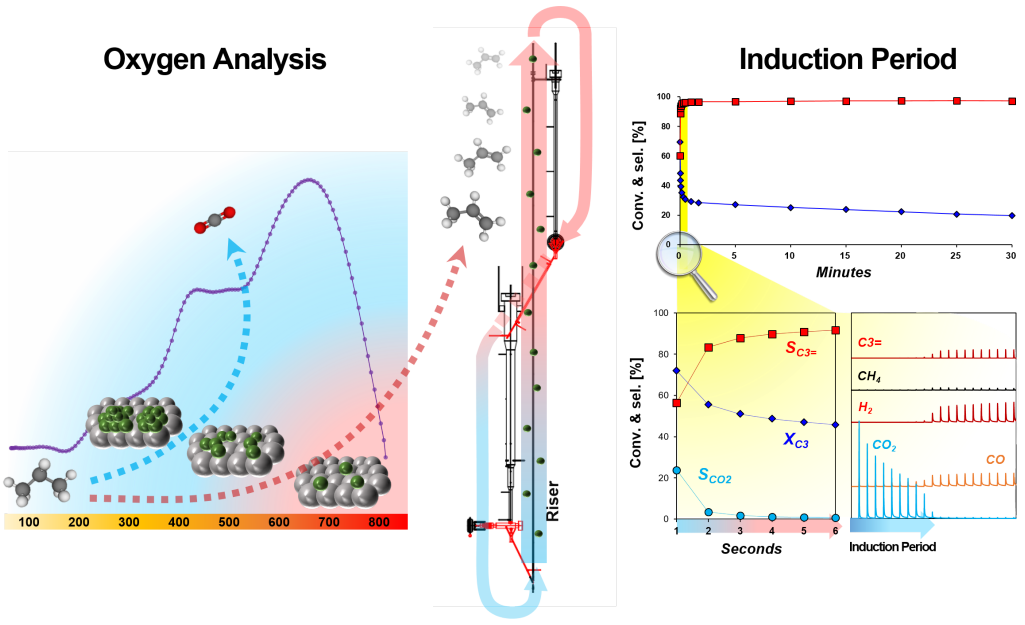

Figure 1. Correlation between induction period and oxygen species of Cr catalyst for fluidized-PDH.

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Kinetic modeling of oxidative coupling of methane over Na_2WO_4 catalyst with various promoters

Yesol Woo[1], Yubeen Jung[1], Seok Ki Kim[1,2], Jeong-Myeong Ha[3,4], Myung-June Park[1,2*]

[1]*Department of Energy Systems Research, Ajou University, Suwon 16499, Republic of Korea*
[2]*Department of Chemical Engineering, Ajou University, Suwon 16499, Republic of Korea*
[3]*Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea*
[4]*Division of Energy and Environment Technology, KIST School, Korea University of Science and Technology, Seoul 02792, Republic of Korea*
[*]*mjpark@ajou.ac.kr*

Keywords: Oxidative coupling of methane, kinetic modeling, parameter estimation, effects of promoters

Introduction. Ethylene is mainly produced by steam cracking of ethane and naphtha. However, this method is the most energy-consuming process and is estimated to emit about 180 to 200 million tons of carbon dioxide [1-4]. For these reasons, many studies have been conducted on developing simpler, cheaper, and more sustainable ethylene production processes. Among them, the oxidative coupling of methane (OCM) is a potential solution for direct ethylene production utilizing natural gas as a substitute for petroleum resources. This study performed experiments over Na_2WO_4 catalyst on silica, where various promoters (Zn, Co, Ce, Cu, Cr, Ni) were adopted. Kinetic models were developed to evaluate the effects of those promoters on reaction pathways and catalytic activity.

Experimental/methodology. The metal-added Na_2WO_4/SiO_2 catalyst with different promoters was prepared with the impregnation method. The experiments were conducted at varying temperatures (725–800 °C), CH_4/O_2 ratio (2–4), inert nitrogen fraction (0.4–0.8), and gas hourly space velocity (10,000–20,000 h^{-1}). Kinetic parameters for lumped kinetic model were estimated by minimizing the objective function, which is the sum of the residuals of square errors of the objective elements. The estimation was performed using the "lsqcurvefit" subroutine in MATLAB (Mathworks, Inc.), where the Levenberg-Marquardt method was applied.

Results and discussion. Simplified reaction pathways were suggested for the OCM reaction. An active O site activates methane (reaction 1), and then ethane is produced by coupling methyl radicals (reaction 2). Produced ethane is converted to ethylene over the active site (reaction 3), and it could be decomposed to CHO radical by thermal or catalytic reaction (reaction 8). Meanwhile, part of the activated methyl radical is converted to CHO radicals (reaction 5) to produce CO (reaction 6) and CO_2 (reaction 7) as a byproduct. For simplified kinetics, pseudo-steady state assumptions were applied to the radicals, and the estimated activation energies for each promoter are as below.

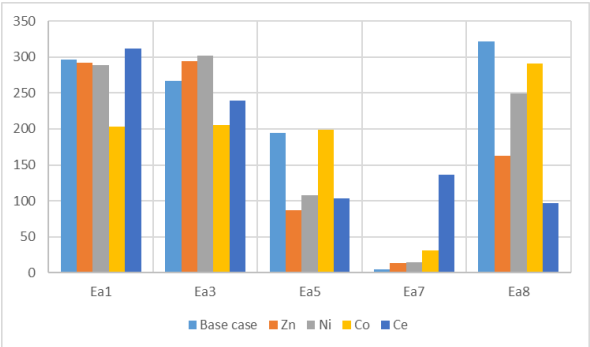

Figure 1. The comparison of activation energies for each promoter.

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Increased stability and activity of Mo/HZSM-5 for methane dehydroaromatization via Nb doping

Stefan Peters[1], Ana de Oliveira Guilherme Buzanich[2], Sebastian Wohlrab[1], Ali M. Abdel-Mageed*[1]

[1] Leibniz-Institut für Katalyse (LIKAT), Rostock, Germany
[2] Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
* ali.abdelmageed@catalysis.de

Introduction: Methane is the world's most abundant hydrocarbon, with large reserves proven as natural gas and methane hydrates (clathrates). High availability, low price and the possibility of renewable biogenic production makes it an attractive C_1 source.[1] The valorization of methane to C-C coupled products like alkenes and aromatics is a "dream reaction" in modern catalysis. Non-oxidative methane dehydroaromatization (MDA) is a promising pathway for the synthesis of benzenoids. Since its inception[2], highly dispersed Mo on porous zeolite materials (primarily HZSM-5) remain the most efficient catalysts for this reaction.[3] Due to the necessarily high reaction temperatures catalyst degradation by carbonaceous deposits ("coking") on active sites and inside pore systems is unavoidable. Improving catalyst stability and regenerability is therefore a pivotal subject for future applications of MDA, for which transition metal dopants have been investigated.[4] In this work we have systematically tested several transition metal dopants for their impact on the catalytic performance of Mo/HZSM-5 catalysts in the MDA reaction, focusing on conversion, product yields, stability on stream and catalyst regenerability.

Experimental/methodology: Studied catalysts were prepared by wet impregnation of NH_4-ZSM-5 supports with aqueous solutions of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ at 25 °C, aiming for 6 wt% Mo. Dopant transition metals (Fe, Co, Zn, Nb; 1 wt%) were introduced via co-impregnation with the respective metal nitrates (or oxalate for Nb). Prepared catalysts were dried and calcined in air at 550 °C for 6 h. Kinetic measurements were performed in a quartz tube reactor at 600-700 °C with a mixture of 90 % CH_4 / 10 % N_2. Reactants and products were quantified using a multichannel GC-MS with N_2 as the internal standard. Oxidative regeneration experiments were performed by *in situ* calcination in air at 450 °C. Catalysts were characterized before and after reaction and after regeneration steps using high-resoution STEM / EDS, XPS, XRD and other analyses. *In situ* XAS at the Mo K-edge was performed at BESSY II (*BAMline* beamline).

Results and discussion: Modification of 6Mo/HZSM-5 with 1 wt% Nb increased the benzene yield at similar methane conversions compared to the unmodified catalyst over 6 h of reaction, while 1Nb/HZSM-5 exhibited no intrinsic MDA activity. By variation of reaction temperature and residence time the positive effect of Nb was further explored: in comparison to 6Mo/HZSM-5, benzene and naphthalene yields for 6Mo1Nb/HZSM-5 were generally increased (by up to 10.4 % and 22.0 %, respectively, at 600 °C). Consecutive reaction / regeneration experiments with both catalysts revealed minor irreversible loss of activity, although superior stability was found for Nb-modified Mo/HZSM-5 in regards to conversion and benzene yield. Through high-resolution STEM coupled with EDS elemental mapping high dispersion and intimate mixing of Mo and Nb was observed in the fresh catalysts. Analysis of *ex situ* and *in situ* NAP XP spectra revealed partial reduction of Mo^{6+} to Mo^{4+} and Mo^{2+}. While Nb^{5+} alone was not reducible under reaction conditions, it was converted to Nb^{4+} and Nb^{2+} species in the presence of Mo. Via *in situ* Mo K-edge XANES analysis in methane atmosphere a retardation of Mo reduction with Nb could be demonstrated, indicating intermetallic oxygen transfer. Further kinetic and analytical results from several characterization methods shall be discussed to explore the effect of Nb on performance and stability of Mo/HZSM-5 catalysts in the MDA reaction.

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Effect of Hydrocracked Vacuum Distillate Addition on FCC Yields

M. Pšenička[1*]

[1]ORLEN UniCRE, Revoluční 1521/84, 400 01 Ústí nad Labem, Czech Republic;
Martin.Psenicka@orlenunicre.cz

Keywords: FCC, HCVD, Alternative feedstock, coprocessing

Introduction. Fluid catalytic cracking units (FCC) are the heart of production within their refineries. Therefore, ways are constantly being sought to further increase the benefit of these cracking units for the future processing of alternative raw materials. Tests with alterative raw materials originating from pyrolysis oils from plastic depolymerization have already been carried out on the FCC simulation unit [1]. and the use of hydrocracked vacuum distillate (HCVD) in co-pyrolysis of Fisher-Tropsh wax vacuum residue [2]. The co-processing of hydrocracked residue on FCC units can bring more possibilities of its use.

Experimental/methodology. Additions of HCVD were chosen at 5, 10 and 20 wt%. It was tested using real raw material for the FCC unit and under real operating conditions on ACE laboratory unit. The resulting product composition is interpolated to constant conversion, constant C/O ratio and constant coke production.

Results and discussion. It was found that with the conversion to a constant production of coke (to maintain the heat balance of the operating unit) with increasing addition of HCVD, a higher total conversion of the raw material occurs and thus a higher production of desired products such as propylene, C_4 olefins and gasoline fraction. The reduction in production of LCO and slurry fraction is just another benefit. These fractions are not very desirable (LCO is mixed into diesel) and the slurry is rather recycled at the FCC unit. A comparison of total conversion as a function of C/O ratio and HCVD addition is shown in Figure 1.

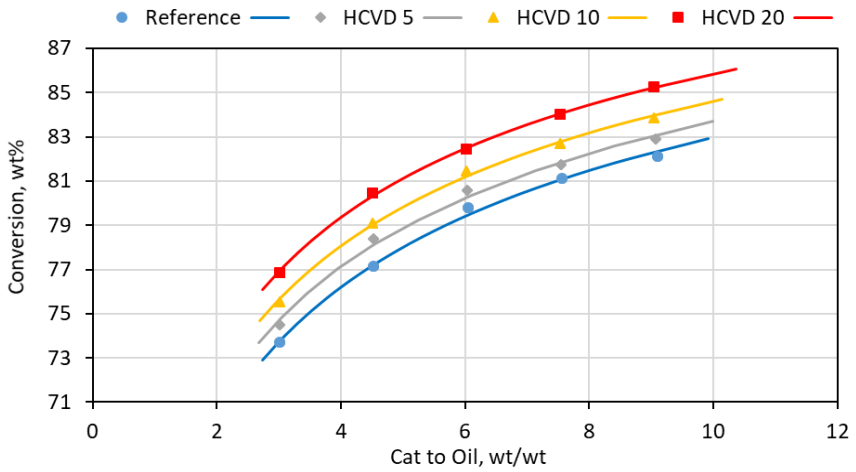

Figure 1 A comparison of the overall conversion

The processing of HCVD at the FCC unit shows only positive benefits and it is therefore at the discretion of the refinery whether it will continue to process HCVD at the FCC unit.

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Influence of electrochemical properties on the catalytic performance of doped NiO catalysts for the oxidative dehydrogenation of ethane

Agustín de Arriba[1], Jose M. López Nieto[1], Ana Dejoz[2], Francisco Llopis[2], Pablo J. Miguel[2], Vicenta González-Alfaro[2], Ramón M. Fernández-Domene[2], Rita Sánchez-Tovar[2], Benjamín Solsona[2,*]

[1]*Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022 Valencia, Spain*

[2] *Departamento de Ingeniería Química, Universitat de València, Av de les Universitats, s/n, 46100 Burjassot, Spain*

[*]*benjamin.solsona@uv.es*

Keywords: oxidative dehydrogenation of ethane, Nb-doped nickel oxide catalysts, electrochemistry.

Introduction. The oxidative dehydrogenation of ethane (ODHE) could be a low demanding energy alternative to produce ethylene. One of the most promising catalytic systems for the ODH of ethane are NiO based catalysts, especially those doped with Nb^{5+}. ODHE on doped NiO catalysts proceeds through a redox mechanism. Therefore, the study of the electrochemical properties of these samples is highly interesting. However, there are just a couple of articles about NiO catalysts that have dealt with the conductivity of p-type semiconductors, and they have related this fact with the catalytic behavior in the ODHE [1, 2]. Then, the aim of this work is to undertake an electrochemical study of doped NiO catalysts to check if a correlation between electrochemical properties and catalytic performance does exist.

Experimental/methodology. Promoted nickel oxides catalysts (with a Ni/Me molar ratio of 9/1) were prepared through evaporation at 90 °C of aqueous solutions of nickel nitrate and metal salts (ammonium niobate (V) oxalate hydrate if Nb is the dopant) with different amount of oxalic acid in the synthesis gel. The solids were calcined in static air for 2 h at 350 or 500 °C. Catalysts were fully characterized by morphological, structural and physico-chemical techniques. Additionally a comprehensive electrochemical characterization using electrochemical impedance spectroscopy, Mott Shottky analysis and cyclic voltametries was carried out.

Results and discussion. According to the obtained results with Nb, the optimal catalysts present n-type semiconductivity, in spite of the fact that the composition (Ni/Nb ratio) is the same for all the catalysts studied. Interestingly, an inverse relationship between the density of non-stoichiometric oxygen and the selectivity towards ethylene has been clearly found in the catalysts presenting p-type semiconductivity. Additionally, the optimal catalysts present high total electrical resistance as a result of the removal of cationic vacancies and electrophilic O- species, which are selective towards the CO_2 formation (Figure 1).

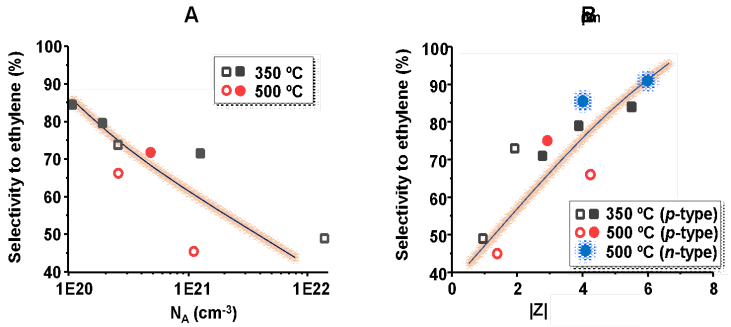

Figure 1. Relationship between the selectivity to ethylene and the acceptor density (A) or the total electrical resistance (B) for Nb-doped NiO catalysts calcined at 350 °C (■) or 500 °C (●,●).Nb-free NiO catalysts (○, □) are also shown. Selectivity to ethylene at isoconversion conditions (10% conversion) and 300 °C.

Acknowledgments

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A Self-Combustion-Depolymerization Approach to Activate Solid-Waste Coal Gangue Minerals for Fluid Catalytic Cracking Catalyst Synthesis

Ye Song, Ruoyu Wang, Xue Yang, Wei Lin*

SINOPEC Research Institute of Petroleum Processing Co., Ltd., Beijing, China
**linwei.ripp@sinopec.com*

Keywords: coal gangue, Y zeolite, solid waste, self-combustion-depolymerization, FCC catalyst.

Introduction.

Globally, explorating efficient utilization technologies for coal gangue, a notorious hazardous solid waste, is one of the most important issues among current sustainable development topics. Herein, a green and energy-efficient self-combustion-depolymerization (SCD) approach is proposed to activate coal gangue into highly reactive silica and alumina species for in-situ crystallization of fluid catalytic cracking (FCC) catalysts[1-3].

Experimental/methodology.

FCC catalysts (SCD-Y) bearing in-situ generated Y zeolites can be readily fabricated via hydrothermal synthesis. In addition to conventional analytical characterization techniques, temperature-distance profiles acquired by a lab-scale drop-tube furnace (DTF) was used to evaluate the self-combustion behavior and the obtained SCD-Y were analyzed by X-ray micro-computed tomography (μ-CT).

Results and discussion.

Taking advantage of the heat released by the self-combustion of coal residue, the SCD activation of kaolin-type CG can be achieved at a medium temperature much lower than that required by natural kaolinite. Using microspheres mainly composed of SCD-CG as zeolization precursors, FCC catalysts bearing in-situ generated Y zeolites (SCD-Y) have been synthesized under hydrothermal conditions, and the zeolite crystals are fully exposed on its external surface. The as-prepared SCD-Y has a high crystallinity of ca. 50 % and a well-developed intraparticle macro-, meso- and microporosity, as revealed by BET, Hg intrusion and μ-CT. A comprehensive dissolving-crystallization microscopic model corresponding to the SCD-Y zeolitization process is proposed on the basis of kinetic study. Significantly, SCD-Y exhibits superior catalytic performance for cracking and prominent anti-deactivation properties for heavy oil conversion, demonstrating a gasoline boosting effect while suppressing dry gas and coke formation. Remarkably, the overall energy consumption (Etot) using this SCD approach (1429.65 kgce/t product) is 33.5% lower than that of the conventional semi-synthesis route (2151.37 kgce/t product). The green synthesis of FCC catalyst can be successfully achieved following this proposed SCD approach, which opens a broad field for energy-saving and high-efficient ultilization of solid-waste coal gangue minerals.

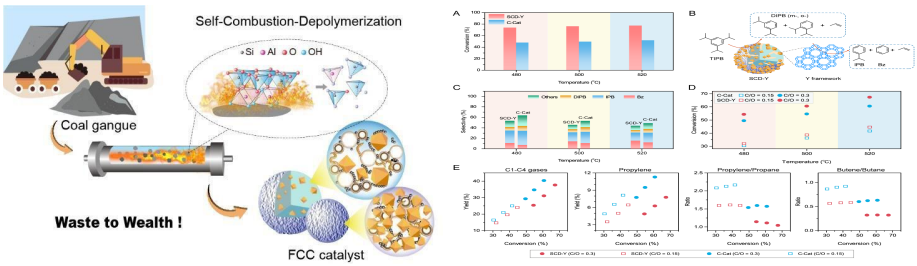

Fig.1 Schematic illustrations of the SCD approach proposed in this work using solid-waste coal gangue as the starting material. Fig.2 Catalytic cracking performances of SCD-Y and C-Cat

Acknowledgments

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Trail of Sulfur during the Desulfurization via Reactive Adsorption on Ni/ZnO

Ye Song, Bo Peng, Wei Lin*

SINOPEC Research Institute of Petroleum Processing Co., Ltd., Beijing, China
**linwei.ripp@sinopec.com*

Keywords: Desulfurization, Ni/ZnO; sulfur transfer, S Zorb; Mechanism.

Introduction.

With increasing number of motor vehicles, the harmful automotive exhaust becomes a major source of pollution in the urban environment all over the world and more stringent environmental legislations have been introduced all over the word. In Euro V and Tier III legislations, sulfur content in gasoline is required to be less than 10 ppm. The S Zorb process has been proved to be effective for the production of low-sulfur gasoline.The single step process is environmentally friendly and consumes significantly less hydrogen and energy, which makes a positive contribution to global carbon emission reduction.

Experimental/methodology.

The RADS mechanism of thiophene on Ni/ZnO sample was studied by a combination of DFT calculation and in-situ experiments. The detailed HYD and DDS pathways of thiophene over Ni (111) were simulated by DFT models. The phase transition during desulfurization process on Ni/ZnO was studied by in-situ XRD and STEM-EDS technology, in order to acquire direct evidence of S-transfer phenomenon between Ni and ZnO.

Results and discussion.

The desulfurization process of thiophene on Ni/ZnO was studied, and the desulfurization mechanism was elucidated. Thiophene molecule is preferentially adsorbed on metallic Ni as π-complexation mode. The desulfurization follows a DDS pathway. Namely, under the reaction conditions, the C-S bond is weakened and split with Ni-S bond formation, and H_2 is spontaneously split into H radicals, leading to the hydrogenation of C atom besides S. This is evidenced by DFT study. After twice of above C-S bond cleavage and following hydrogenation, the S-free C4 olefin is formed and can be further hydrogenated, while the sulfur is retained on the Ni surface, forming Ni_3S_2 phase. The resulted Ni_3S_2 phase after desulfurization, which is in close vicinity with ZnO phase in a typical S Zorb catalyst, undergoes a sulfur-transfer towards ZnO. As a consequence, the Ni active site is recovered and the sulfur moves towards ZnO, forming ZnS phase. Efficient sulfur-transfer is achieved at the interface of Ni/ZnO materials with the presence of H_2. This is demonstrated by a multi-technique characterization of in-situ XRD, STEM and EDS mapping. For the S Zorb process which has been widely applied in large scale, the current study is specifically meaningful, it provides convincing evidences of the essential materials transformation during practical operation.

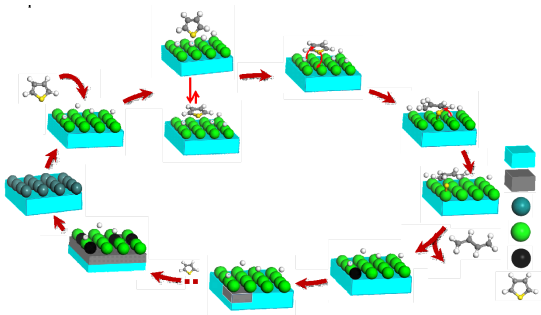

Fig.1 Scenario of reactive adsorption desulfurization process of thiophene on Ni/ZnO

Acknowledgments

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Naphtalene-rich industrial aromatic oils as alternative liquid hydrogen carriers: hydrogenation studies

P. Rapado-Gallego[1], E. Díaz[1*], J.I. Fidalgo-Martínez[2], E. Sánchez-Cortezón[2], S. Ordóñez[1]

[1]*Department of Chemical and Environmental Engineering, University of Oviedo, Oviedo, Spain*
[2]*Química del Nalón, S.A., Oviedo, Spain*
[*]*diazfeva@uniovi.es*

Keywords: LOHCs, hydrogenation, noble metal catalysts

Introduction.

Liquid organic hydrogen carriers (LOHCs) are promising materials for hydrogen chemical storage, with similar properties than liquid fuels [1]. However, most of the proposed LOHCs are either pure compounds or model mixtures of aromatic compounds. The use of industrial oils enriched in aromatic compounds will be of key interest in these technologies. The hydrogenation of two carbochemical industrial oils containing large amounts of polyaromatics has been studied in this work, comparing the results with the obtained with a commercial aromatic fluid (Solvesso™ 200, Exxon Mobil). All of them contain naphthalenes and methylated derivatives, which are solid at ambient conditions, but easily solved for easier operation [2].

Experimental/methodology.

The reactions have been carried out in a stainless steel autoclave reactor of 50 mL total volume at temperatures of 150 and 250 °C. The volume used in all reactions was 30 mL. 5 % Pt/Al_2O_3 and Pd/Al_2O_3 reduced catalysts (Sigma-Aldrich), 1.5 g, were introduced into the reactor. After an evacuation in N_2, the media was pressurized until 50 bar and recorded its evolution for the 24 hours of reaction. Final products were analyzed in a gas chromatograph equipped with a mass spectrometry (Agilent Technologies 7890B).

Results and discussion.

Table 1 shows the content of the three oils, being included in methylnaphthalne derivates, 1-methylnaphthalene, 2-methylnaphthalene and their derivates. Likewise, Oil B presents quinoline in its composition. Oil A and Solvesso 200 are free of sulfur compounds, whereas Oil B presents a content < 0.7 %.

Table 1. Composition of the three considered aromatic oils.

	Naphthalene	Methylnaphthalene derivates	Quinoline	Others
Oil A	12.28 %	32.92 %	-	54.80 %
Oil B	5.25 %	56.29 %	7.07 %	31.39 %
Solvesso 200	6.79 %	72.18 %	-	21.03 %

Naphthalene and methylnaphthalenes do not hydrogenate at all, for any catalyst or temperature, in the case of Oil A and Oil B, whereas Solvesso 200, at 150 ºC, reaches a conversion around 20 % and, at 250 ºC, over 70 % for naphthalene and derivates for both catalysts, without observing substantial differences between the two oils. Quinoline of Oil B reacts easily to form tetrahydroquinoline, in fact, at 150 ºC for Pt/Al_2O_3 the conversion is already complete, and for the Pd/Al_2O_3, a value of 80 % is reached. These results suggest, add to the extraordinary reactivity for hydrogenation of quinoline, the possible interference in hydrogenation of heavy compounds, mainly of aromatic nature, which are present both in Oil A and Oil B, whereas Solvesso 200 is free of these heavy compounds. Our results suggests that that oils containing light aromatic (up to two fused cycles) and nitrogenated aromatic compounds are promising LOHCs, whereas the presence of larger polyaromatic compounds hinders this property.

Acknowledgments
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Pablo Rapado acknowledges the Spanish Ministry of Education for the PhD grant (PRE2021-097871).

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Application of AI-based models integrated with Ensemble ML paradigms for simulating light olefins yield in crude-to-chemicals conversion

A. Tanimu[1*], A. G. Usman[2], H. Alasiri[1,3], A. Aitani[1]

[1]*Center for Refining and Advanced Chemicals, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*

[2]*Department of Analytical Chemistry, Faculty of Pharmacy and Operational Research Centre in Healthcare, Nicosia, TRNC, Turkey*

[3]*Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*

[*]*abdulkadir.tanimu.1@kfupm.edu.sa*

Keywords: ethylene, propylene, AI-models, crude oil, cracking

Introduction. Demand for petrochemical feedstocks has been steadily increasing due to the growing demand of petrochemical intermediates that serves as raw materials in the production chain of many industries [1]. The light olefins, particularly ethylene and propylene are important part of these petrochemical feedstocks that have seen increasing demand in recent time [2]. Therefore, with careful optimization of crude oil feed and cracking conditions, the yield of light olefins can be maximized while lessening the yield of dry gas and coke. However, this approach involves handling large number of variables that are ordinarily difficult to process using simplified/physical models. The re-emergence of artificial intelligence (AI) in the early 21st century has made analysis, prediction and optimization of large number of variables in various academic and industrial application much easier and less laborious [3]. This study utilizes the application of four stand-alone AI techniques for modeling the yield of ethylene and propylene in the catalytic cracking of crude oil feeds using temperature, feed, conversion (%), total gas, dry gas and coke as the independent variables. Additionally, four Ensemble paradigms were developed to further improve the performance accuracy of the stand-alone paradigms.

Experimental/methodology. The catalytic cracking reaction was carried out according to the ASTM D-7964 method in an Advanced Catalytic Cracking (ACE) unit. The prediction of the MLs models was done on MATLAB (2017b). Correlation matrix and non-linear sensitivity analysis were conducted to filter the input combinations into three different classes (M1, M2 and C3) based on the dependent-independent variables relationship. Prediction performance was evaluated basaed on Co-efficient of determination (R2), Pearson correlation co-efficient (PCC), Mean squared error (MSE) and Root mean squared error (RMSE)

Results and discussion. Results of the stand-alone models at certain instances showed weak performance accuracy while the Ensemble paradigms depicts that these techniques can improve the performance of the single models up to 58% and 62% in the calibration and validation phases respectively as shown in figure 1.

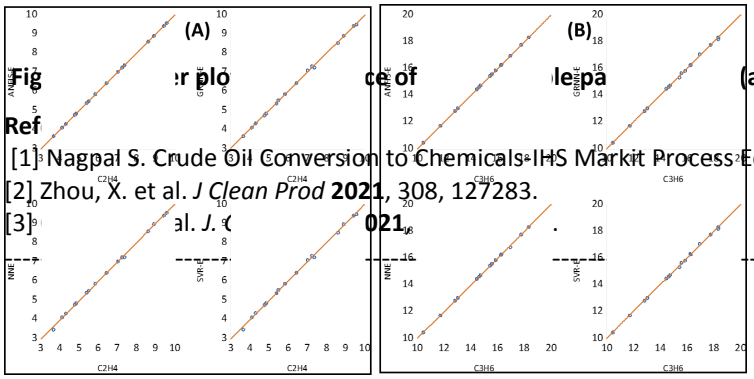

Fig r plo ce of lepa (a) C_2H_4 and (b) C_3H_6 yield modeling

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Chemical recycling of waste P-F resins and particle boards by fast catalytic pyrolysis towards value-added chemicals and fuels

S.M. Kavoukis[1], C. Pappa[1], S. Torofias[1], P. Soldatos[1], A. Margellou[1], K.S. Triantafyllidis[1,2,*]

[1] *Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece*
[2] *Centre for Interdisciplinary Research and Innovation (C.I.R.I.), AUTH, Thermi 57001, Greece*
**ktrianta@chem.auth.gr*

Keywords: PF resins, waste particle boards, fast (catalytic) pyrolysis, chemical recycling

Introduction

Within the concept of circular (bio)economy, the chemical recycling and valorisation of organic wastes, such as plastics, polymers and related composite products, e.g. used furniture, etc., is a promising solution towards renewable fuels, chemicals and polymers. Thermochemical methods (combustion, gasification, pyrolysis) are proven to be efficient methods in recovering bio-energy and chemicals from waste biomass and plastics. Fast pyrolysis leads to enhanced production of liquid products (bio-oils) which however may contain oxygenated compounds (i.e. acids, furans, ketones, phenolics, etc.) in the case of lignocellulosic biomass wastes and related bio-based resins and wood-composite products [1,2]. These bio-oils can be either used to extract individual group of compounds, such as phenolics, to be utilized as monomers for the production of the original or other relevant adhesive resins or can be upgraded via deoxygenation and aromatization reactions over acidic catalysts to BTX aromatic compounds [3,4].

Experimental/methodology

In the present work we have investigated the fast (catalytic) pyrolysis of vine pruning (in the form of wood chips that are used to form the particle board), cured phenol-formaldehyde (PF) resin solids (used as adhesive in the particle board) and the particle board itself made from the PF resin and the vine pruning chips. The experiments were conducted on a lab-scale fixed bed pyrolysis reactor, using silica sand as the inert heat carrier at 400, 500 and 600°C (for non-catalytic pyrolysis) or a ZSM-5 zeolite catalyst for in-situ upgrading of the pyrolysis vapors at 500 and 600°C. Liquids, solids and gases were collected for analysis with GC-MS, GC-FID, NMR, etc. Additional fast pyrolysis experiments were performed on a Py/GC-MS system to investigate the relative composition of the pyrolysis vapors.

Results and discussion

The fast pyrolysis of vine pruning provided 30-50 wt.% bio-oil, 25-35 wt.% solids/char and 10-25 wt.% gases, depending on process temperature. The obtained bio-oil comprised mainly of alkoxy-phenols as well as carboxylic acids, esters and ketones. The pyrolysis products of the cured PF resin solids were 10-25 wt.% bio-oil, 60-80 wt.% solids and 2-10 wt.% gases, with bio-oil containing mainly phenol as well as some aromatic compounds. The respective particle board resulted in 30-55 wt.% bio-oil, 20-35 wt.% solids and 10-25 wt.% gases, with the bio-oil containing mainly alkyl-phenols, as well as alkoxy-phenols, carboxylic acids and esters. The above results indicate that the fast pyrolysis of particle boards is indeed a combination of the mechanisms/products that apply in the pyrolysis of the vine pruning chips (lignocellulosic biomass) and cured PF resin alone. Especially the PF resin derived oil can provide pure (alkyl)phenols that can be utilized back into the production of PF resins with the same or similar properties. With the use of the acidic zeolite catalyst, the obtained bio-oils were enriched in BTX mono-aromatics and naphthalenes, being also useful in the chemicals/polymer industry and refineries, via decarbonylation, decarboxylation, dehydration/ dehydroxylation, cracking, dealkylation and aromatization reactions of the intermediate oxygenated/ phenolic compounds formed by thermal pyrolysis.

Acknowledgements

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Investigating mode switches in a hydrotreater through mathematical modelling

J. Venuti Björkman[1,2], T. Belkheiri[1], L. J. Pettersson[2], E. Kantarelis[2]

[1]*Process Technology, Nynas AB, Nynäshamn, Sweden*
[2]*KTH Royal Institute of Technology, Department of Chemical Engineering, Stockholm, Sweden*
[*]*jacob.venutibjorkman@nynas.com*

Keywords: trickle bed reactor, hydrodenitrogenation, HDN, hydrodearomatization, HDA, adsorption

Introduction. One of the key processes to produce lubricant base oils is hydrotreatment over metal sulfide catalysts to remove the polyaromatic hydrocarbons and other compounds. The hydrotreating reactor is continuously operated producing different products from feedstocks of varying composition. Shifting between products (mode switch), can be impacted by memory effects of the catalyst which in turn affects the subsequent production [1,2]. Organic nitrogen compounds present in the feedstocks are considered to be partly responsible for this effect [3]. In this work, a dynamic mathematical model of a trickle bed reactor is developed to evaluate catalysts during a mode switch.

Experimental/methodology. Step response experiments were carried out in a microflow trickle bed reactor operated at 120 barg and between the temperatures 280 to 320 °C using sulfided NiMo catalysts. The model reaction was the hydrogenation of phenanthrene, a cata-condensed triaromatic hydrocarbon. The organic nitrogen compounds (carbazole and acridine, representing non-basic and basic nitrogen compounds, respectively) introduced in the step response. Tracer experiments were performed to estimate the residence time distribution (RTD) to differentiate the dispersion caused by the reactor, interaction with the catalyst, and tubing and gas-liquid separator. The RTD of the reactor itself was modelled using the Piston Dispersion Exchange (PDE) model and the tubing together with the gas-liquid separator was modelled using a combination of tank-in-series (TIS) and plug flow reactor (PFR) models.

Results and discussion. In Figure 1, two kinds of mode switches are presented: the introduction (deactivating mode switch) and the removal of (reactivating mode switch) of carbazole. When carbazole is introduced, the conversion of phenanthrene is lowered due to competitive adsorption of the hydrogenation sites. Moreover, during the reactivating mode switch, there is a time delay in the when the phenanthrene conversion is back at its initial value. This illustrates that the developed model system replicates the memory effect observed in full-scale hydrotreaters.

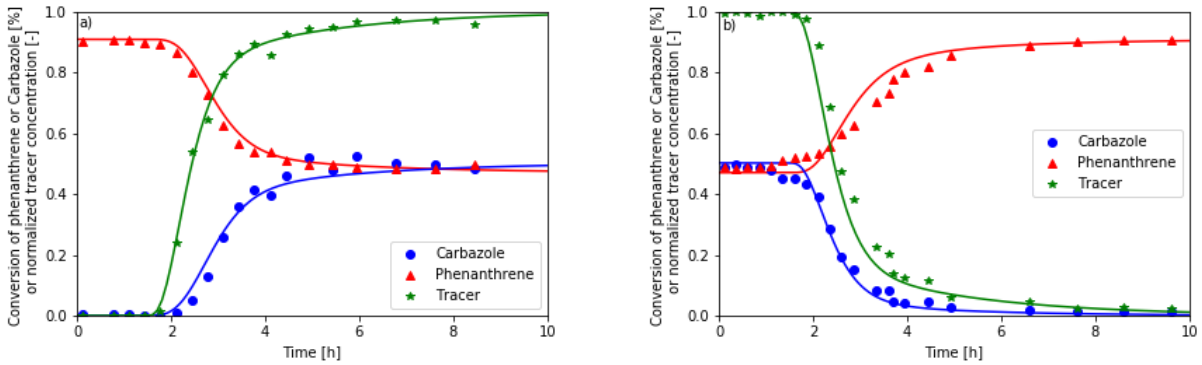

Figure 1. Effect on the dynamic conversion of phenanthrene upon a mode switch with carbazole. The introduction(a) and the removal (b) elution profiles of carbazole, phenanthrene, and tracer(dodecane) as a function of time. The data points are the experimental observations while the lines represent the fitted model. Experimental conditions: 300 °C and 120 barg.

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High Pressure Ring Opening using supported NiWMo catalysts

C. Gross[1], R. Khare[1], J.A. Lercher[1*]

[1]*Department of Chemistry and Catalysis Research Center, TU München, Garching 85748, Germany*
[*]*johannes.lercher@tum.de*

Keywords: high pressure, Ring opening, Decalin, mixed metal sulfides

Introduction. The interest in investigating the removal of polynuclear aromatics from fuel has steadily increased over the last few decades as an effort to decrease fossil fuel's environmental impact. Decreasing the fraction of naphthenic molecules with selective ring opening is also an important step to upgrade low-value crude oil and streams stemming from refineries. Commercially available catalysts for ring opening reactions usually contain hydrogenating agents based on one or more noble metals, supported on an acidic support. Common examples of such catalysts are iridium or platinum, supported on various aluminosilicates. Despite their decent ring opening capabilities, these catalysts are highly sensitive to sulfur in the feed, showing severe decrease or even complete halt of ring opening reactions at sulfur levels as low as 20 ppm.[1] In this work, we investigated supported metal sulfides, which show high selectivity towards ring opening without the need for noble metals and exhibit a high tolerance toward sulfur in the feed.[2]

Experimental/methodology. The influence of the metal composition, as well as pressure, temperature, and conversion, on the selectivity towards ring opening of decalin have been investigated. To achieve this, a series of SiO_2-supported mixed metal catalysts containing nickel, tungsten, and molybdenum were prepared by impregnating SiO_2 with an aqueous solution of their respective metal salts: $(Ni(NO_3)_2{\cdot}6\ H_2O$, $(NH_4)_6H_2W_{12}O_{40}{\cdot}x\ H_2O$, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O)$, followed by drying and calcining in a flow of synthetic air for 5 h at 773 K and a subsequent *in situ* sulfidation. The synthesized catalysts were characterized by AAS and IR spectroscopy. Ring opening was performed in a trickle bed reactor, pressurized to 160 bar. In a typical experiment, approximately 150 mg of catalysts were diluted with 350 mg SiC and loaded in the reactor. After an initial drying step in a flow of H_2, the catalysts were sulfided using a mixture of heptane and dimethyl disulfide (DMDS) with a total sulfur concentration of 3 wt.% in a flow of H_2. Following the sulfidation step, the liquid feed was changed to a mixture of decalin and DMDS with a total sulfur concentration of 0.1 wt.%.

Results and discussion. We report that the conversion, as well as the selectivity towards ring opened products, is influenced by the ratios of the respective metals. Based on the results of our experiments, the ideal ratio appears to be 10, 30, and 15 wt.% of Ni, W, and Mo respectively, and a deviation from these metal loadings led to a decrease in both conversion of decalin as well as selectivity towards ring opening. Our experiments also show, that for ring opening of decalin to occur, an initial (skeletal) isomerization step is necessary. Only after this primary isomerization, the secondary ring opening reaction can occur. Temperature and liquid hourly space velocity variations showed that an equilibrium of hydrogenation and isomerization reactions is achieved at a conversion of ~15%. Additionally, dehydrogenation towards tetralin (and subsequent naphthalene formation) occurs as a side reaction but can be minimized at elevated pressures above 150 bar. Our experiments also suggest that the ring opening of decalin is highly pressure dependent, as we observe a significant increase in the selectivity toward ring opening with increasing pressure, while we see a sharp drop in the formation of dehydrogenated products. The selectivity towards isomerized and cracking products stays virtually unchanged over the entire investigated pressure range.

Acknowledgments
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Ligand-free Cr-catalyzed ethylene dimerization in an ionic liquid-organic solvent biphasic system with 100% 1-butene selectivity

Nguyen Thi Kim Chau[1], Hyo Jun Lee[2], Minjae Lee[2], Young-Min Chung[1*]

[1]*Department of Chemical Engineering, Kunsan National University, 558 Daehak-ro, Kunsan, Jeollabuk-Do 54150, Republic of Korea*
[2]*Department of Chemistry, Kunsan National University, 558 Daehak-ro, Kunsan, Jeollabuk-Do 54150, Republic of Korea*
[*]*Corresponding Author's E-mail address (ymchung@kunsan.ac.kr)*

Keywords: ethylene dimerization, ionic liquid, two-phase reaction

Introduction.

1-Butene is one of the important basic chemicals that belongs to the family of linear alpha olefins (LAO). While a number of technologies have been addressed for 1-butene production using different metal-complex catalysts, intensive separation processes are required to separate the 1-butene from other isomers and hydrocarbons with different chain length.

In this work, we report facile and recyclable ligand-free Cr-catalyzed ethylene dimerization in an ionic liquid-organic solvent biphasic system with 100% 1-butene selectivity. The unprecedented perfect α-olefin selectivity without polymer formation may offer promising opportunity for elucidation of highly efficient dimerization process without complicated and energy-intensive by-products separation processes.

Experimental/methodology.

A range of ionic liquids were synthesized by using two cations (1-octyl-3-methylimidazolium and 1-decyl-3-methylimidazolium) and three anions (Tf_2N^-, BF_4^-, and PF_6^-). Ethylene dimerization was performed in an IL-toluene biphasic system using a high-pressure reactor by using Et_2AlCl or MMAO as an activator.

Results and discussion.

As shown in Table 1, with Et_2AlCl, catalytic activity and 1-butene selectivity were reached as high as 1405 g/gCr.h and 92.6 wt%, respectively (Entry 4). Furthermore, 100% 1-butene selectivity was obtained in the presence of MMAO (Entry 6). The uncontrollable polymerization proceeded (98% of PE) in the absence of IL (Entry 1) strongly implies the crucial role of IL in regulating the chain growth.

The extremely high 1-butene selectivity can be rationalized in terms of low solubility of hydrocarbons in IL [1]. It is assumed that the 1-butene formed by the first dimerization will no longer participate in the successive oligomerization, and transfer to organic phase immediately. This unique reaction environment is beneficial in maximizing 1-butene selectivity.

Table 1. Ethylene dimerization promoted by Cr catalyst under various reaction conditions

Entry	M/L/A (mole ratio)	Activator	Ionic Liquid	TOF (g/gCr.h)	Selectivity (wt%)		
					1-C4 (C4)	1-C6+ (C6+)	PE
1	1/0/300	Et_2AlCl	-	1514	3.8(4.2)	n.d.	95.4
2	1/0/300	Et_2AlCl	$C_1C_{10}Im$-Tf_2N	2270	0.8 (1.2)	n.d.	98.0
3	1/0/300	Et_2AlCl	$C_1C_{10}Im$-BF_4	1298	83.2 (100)	-	-
4	1/0/300	Et_2AlCl	$C_1C_{10}Im$-PF_6	1405	92.6 (96.8)	0.5 (3.2)	-
5	1/1/300	Et_2AlCl	$C_1C_{10}Im$-PF_6	1514	96.0 (100)	-	-
6	1/0/300	MMAO	$C_1C_{10}Im$-PF_6	1624	100 (100)	-	-

Acknowledgments

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SYNTHESIS OF HIGH-OCTANE GASOLINE ADDITIVES ON CATALYTIC "INTELLIGENT SYSTEMS"

K. Kadirbekov, O. Yugay, A. Serebryanskaya, G. Abdiyusupov, S. Zholdybaev, Tusipkaliev E.

[1] *JSC A.B. Bekturov Institute of Chemical Sciences, Almaty, Kazakhstan*
E-mail: kkairati@mail.ru

Methyl tert-butyl ether (MTBE) and ethanol were found the most widespread usage among oxygen-containing additives for gasoline. However foreign experience in the use of MTBE and ethanol in the composition of gasoline has revealed a number of problems. These include, for example, the harmfulness of MTBE and a possible ban on the production of gasoline containing this additive or the phase instability of gasoline-ethanol fuels. In recent years, the world's existing MTBE production facilities have been converted to the production of ethyl tert-butyl ether (ETBE) [1, 2].

Catalytic systems obtained by depositing polymer-metal complexes on solid inorganic supports are the most promising catalysts in alkylation reactions. The principle of operation of such catalysts is similar to the so-called "smart systems" (intelligent systems), where polymer ligands fix metal complexes on the surface, but at the same time retain relative structural mobility and have high catalytic activity.

In the ETBE synthesis reaction, the catalytic properties of a new "smart system" nanometal-polymer/natural zeolite were studied. In this communication, the features of the synthesis of ETBE by the interaction of bioethanol with isobutylene on the Mo-Polymer/HCL catalytic system are considered. HCL is acid-activated natural zeolite (Kazakhstan) with the mineral phase clinoptilolite. The polymer was applied on HCl in an amount of 0.5–1.0 wt%. The influence of the nature of the component of the composition of a catalytically intelligent system and process parameters on the yield of ETBE was investigated.

According to chromatographic analysis, the reaction mixture contains the main product ETBE, isobutylene, ethanol, methyl ethyl alcohol, 2-methoxy-2-methylpropane, ethyl propyl ether, 2,4,4-trimethyl-pentene-2, 2,3,4,5- tetramethylhexadiene and other hydrocarbons. A detailed review of all the by-products resulting from the alkylation of bioethanol with isobutylene showed that heavier and more branched compounds are obtained at elevated process temperatures. The maximum yield of ETBE was obtained at 70°C. An increase in the volume of the catalyst positively affects the increase in the yield of ETBE, at which the yield of the target product reaches 76%. This is due to the relatively long contact time of bioethanol and isobutylene vapors with the catalyst surface. The lowest ETBE yield is observed at a temperature of 50°C – 10% due to the fact that alcohol and gas vapors did not have time to reach the refrigerator, but began to condense even upon contact with the catalyst. With an increase in temperature to 90°C, a decrease in the yield of ETBE to 32% is observed due to the formation of heavier compounds. Thus, it can be concluded that maintaining the required temperature and stable contact of the vapors with the catalyst is an important factor in achieving a high yield of ETBE.

Compositions prepared from reaction mixtures with ETBE were added to A-80 commercial gasoline with the following initial octane data: RON (Research Octane Number) = 84.8; MON (Motor Octane Number) = 79.9 and AKI (Anti-Knock Index) = 82.3. Tests have shown that the highest octane number of 96.6 is observed when adding a composition with 8.33% ETBE, obtained at a temperature of 70°C. This indicates the technological and environmental efficiency of using compositions based on ETBE as a high-octane additive to gasoline.

Acknowledgments *The Research was funded by the Science Committee of MSHE of Kazakhstan (BR10965255 and BR18574042).*

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Aromatic admixture effect on alkane hydrocracking over Pt/HUSY

N. Korica[1], B. A. Canudo[1], P.S.F. Mendes[1 $], J. De Clercq[2], J.W. Thybaut[1*]

[1]*Laboratory for Chemical Technology, Ghent University, Technologiepark 125, B-9052 Ghent, Belgium*

[2]*Industrial Adsorption and Catalysis Technology, Ghent University, Valentin Vaerwyckweg 1, B-9000 Ghent, Belgium*

[*]*Corresponding Author, e-mail: Joris.Thybaut@UGent.be*

[$]*Present address: Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal*

Keywords: hydrocracking, aromatics, hydrogen excess, total pressure effect

Introduction

Hydrocracking of saturated hydrocarbons occurs on a bifunctional catalyst, containing metal and acid sites, via unsaturated intermediates [1]. In addition to (cyclo)alkanes, aromatic molecules represent a significant fraction in hydrocracking feeds, both in conventional ones as in renewable, bio-based ones. The reaction network of aromatic molecules over a bifunctional catalyst [2] includes hydrogenation to cycloalkanes and direct acid catalyzed reactions, which are clearly distinct from those for (cyclo)alkanes. This specific feature of aromatics may result, depending on operating conditions, in a more prominent admixture impact in contrast to cycloalkanes on alkane hydrocracking [3]. The goal of this work is to analyse this impact on *n*-alkane hydrocracking and suggest mitigation measures.

Experimental

The toluene admixture impact was experimentally assessed over 0.3 wt%Pt/HUSY (with SiO_2/Al_2O_3 molar ratio of 12), which was previously confirmed as a well-balanced catalyst for *n*-octane hydrocracking [4]. The experiments were carried out using the high-throughput kinetics setup for mechanistic investigations with pure *n*-octane and the feed containing 20 mol% toluene. The present work focuses on the interplay between toluene admixture effect, H_2-to-hydrocarbon (H_2/HC) molar ratio (6.5-200) and total pressure (10-20 bar), and consequently these parameters were primarily varied. Nitrogen was added as a diluent to keep *n*-octane partial pressure constant (0.1 bar). The catalyst stability was analyzed over more than 3 h time on stream.

Results and discussion.

The impact of toluene admixture and hydrogen excess on catalyst stability is shown in Figure 1. While at high H_2-to-hydrocarbon ratio, no impact of toluene on *n*-octane conversion was observed, toluene effect was obvious when H_2/HC ratio was decreased to 6.5. At high H_2 excess hydrogenation of toluene dominates over the reactions which lead to deactivation - only methylcyclohexane and its isomers are found as toluene products. On the other hand, a negative impact of toluene on the catalyst stability was observed at lowered H_2/HC ratio.

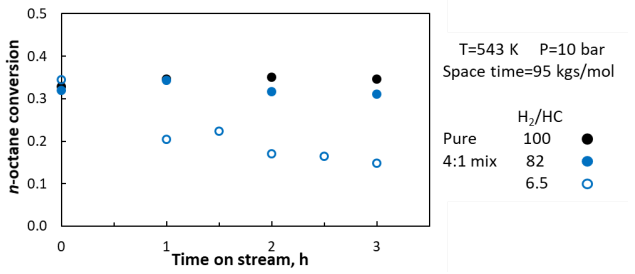

Figure 1 *n*-Octane conversion when fed pure and in 4:1 n/n mixture with toluene as function of time on stream: impact of H_2/HC molar ratio

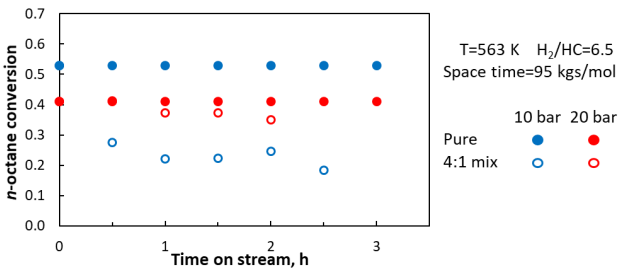

Figure 2 *n*-Octane conversion when fed pure and in 4:1 n/n mixture with toluene as function of time on stream: impact of total pressure

Figure 2 compares impact of toluene admixture at 6.5 molH_2/molHC at two total pressures. The catalyst deactivation was more prominent at lower total pressure (and lower nitrogen dilution). At higher pressure and nitrogen dilution, bimolecular reactions of toluene on acid sites leading to coke precursors were less likely. In conclusion, the negative admixture impact of aromatics can be mitigated by increasing the hydrogen excess and/or total pressure.

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Supported Iron Nanoparticles as sustainable Catalysts for the selective Acetylene Hydrogenation under industrial Front-End Conditions

Hannah Lamers[1], M. Lucas[2], M. Rose[3*]

[1, 2, 3]*Technical University of Darmstadt, Darmstadt, Germany*
[*]marcus.rose@*tu-darmstadt.de*

Keywords: Heterogenous catalysis, acetylene hydrogenation, supported iron nanoparticles.

Introduction. Ethylene is one of the most important monomers for polymer production and is needed in high purity to guarantee reproducible product qualities in olefin-based polymers. Since multi unsaturated impurities, such as acetylene, coming from petroleum-based ethylene sources lead to catalyst poisoning in polymerization reactions, the generation of ethylene-rich streams with acetylene concentrations lower than 1 ppm are urgently necessary.[1,2] State of the art catalysts for the selective acetylene hydrogenation are alumina supported palladium silver alloyed nanoparticles.[3] Owing to high palladium prizes and low availability, innovative and sustainable catalyst systems are needed. Iron-based catalysts are highly promising substitutes due to the high natural occurrence, the non-toxicity and the known hydrogenation-activity.[2] In preliminary studies the suitability of zero-valent iron catalysts was proven by using unsupported α-Fe nanoparticles showing very high activity and selectivity in the semi-hydrogenation of acetylene.[2] To further enhance catalytic activity by modifying the particle size, the surface area and the metal dispersion, different alumina supported iron nanoparticles are currently investigated.

Experimental/methodology. The supported iron nanoparticles are synthesized via incipient wetness impregnation on alpha-alumina using different iron precursors as well as varying metal loadings. All catalyst precursors are calcinated and subsequently reduced to the zero-valent iron species before use. The supported iron catalysts are analyzed via X-ray diffraction (XRD), N_2-physisorption and X-ray fluorescence spectroscopy (XRF) as well as temperature programmed reduction (TPR). The catalytic testing of the supported iron nanoparticles is carried out in a continuous flow fixed-bed reactor with a modeled feedstock composition of industrial acetylene removal units under front-end conditions.[4,5] In a typical reaction sequence, 200 mg of catalyst are used, and the temperature is varied between 40 °C and 90 °C. The reaction is monitored via online GC resulting in high-resolution conversion- and selectivity-profiles.[5]

Results and discussion. Alpha-alumina supported catalysts with 1 %, 5 % and 10 % iron loading, respectively, were successfully synthesized, and the iron content was monitored via XRF. The reduction profiles of the supported iron catalysts were determined via TPR and indicate full reduction to Fe^0 at 900 °C. In a first attempt, the catalyst with 10 % iron loading is applied in the semi hydrogenation of acetylene. The temperature was varied between 40 °C and 90 °C in 10 °C intervals. At 90 °C the conversion is at 58.76 % and decreases with a decline in temperature. The produced amount of ethane is low at all temperatures intervals, indicating neither significant acetylene over hydrogenation nor ethylene hydrogenation. The results demonstrate that the alumina supported catalyst with 10 % iron loading shows excellent activity and very high selectivity at 90 °C as well as very good stability over time. These results underline the suitability of iron catalysts as very promising sustainable alternatives to conventional palladium-based materials. More investigations are needed to reveal the correlation between the metal loading and the catalysts activity. Moreover, the influence of carbon monoxide as selectivity directing agent and the influence of bimetallic compounds on the activity and selectivity needs to be determined to further improve the catalytic performance of alumina supported iron-based nanoparticles.

Acknowledgments. *We gratefully acknowledge the financial support by the collaborative research center "Iron, upgraded!" (CRC 1487).*

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Synergistic shape selectivity of H-Beta and H-ZSM-5 in heavy aromatics hydrocracking for xylene-rich BTX

Jinho Oh, Jung Kyoo Lee*

Chemical Engineering (BK21 FOUR Graduate Program), Dong-A University, Busan 49315, South Korea
**jklee88@dau.ac.kr*

Introduction.

Due to global climate change and environmental concerns caused by the increased carbon emissions from fossil fuels use, the demand for oil-derived fuels such as diesel and marine heavy fuel oil will decrease in the future. Hence, the disposal of polycyclic aromatics (PCA) by-products of diesel-boiling-range, being produced in large quantity from oil and petrochemical processes, would be a problematic issue. Therefore, the catalytic conversion of PCAs into high-value products is of great concern. One feasible option for upgrading the surplus PCAs is to produce high-value benzene/toluene/xylenes (BTX) by hydrocracking [1]. The hydrocracking of PCAs in principle gives BTX along with naphtha-range cracking products [2,3] which can be fed to naphtha cracker for light olefins or blended into gasoline pool.

Experimental/methodology.

Herein, we report a highly selective hydroconversion of PCAs obtained from a commercial aromatic complex, C_{10}^{+} heavy aromatics, into BTX rich in xylenes. We tested two different processes, a direct HYC and selective hydrogenation (HYD) followed by HYC, by using a fixed-bed down-flow micro-reactor under a moderate pressure (40 bar). For the selective HYD of C_{10}^{+} heavy aromatics, we employed a $Mo_2C/\gamma\text{-}Al_2O_3$ as the catalyst. For the HYC catalyst, various metals were supported on H-Beta (B) or hybrid zeolite mixture of H-Beta and H-ZSM-5 (Z) (BZ hereafter). We found that the two step process consisted of selective HYD followed by HYC can give much higher per-pass yield of BTX than the direct HYC. More importantly, it was found that the hybrid zeolite mixture, BZ in the HYC catalyst, can exhibit a synergistic shape selectivity in the hydrocracking of PCAs leading to a high per-pass yield of BTX rich in xylenes.

Results and discussion.

Fig. 1a shows that HYC catalyst containing BZ gave much higher yield of BTX than that containing B only, whereas ethylbenzene and C_9-C_{10} aromatics yield was in opposite as shown in **Fig. 1b**. Over the HYC catalyst with BZ, xylenes were formed in the largest amount among BTX due to the transalkylation reactions described in **Fig. 1c**. More detail results and the synergistic shape selectivity brought by H-Beta and H-ZSM-5 will be discussed.

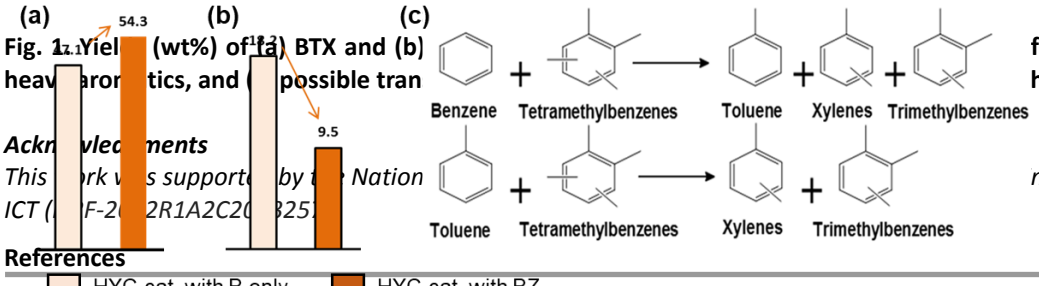

Fig. 1. Yield (wt%) of (a) BTX and (b) heavy aromatics, and (c) possible transf pre-hydrogenated C_{10}^{+} h xylenes selectivity.

Acknowledgments

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The conversion of aliphatic hydrocarbons to aromatics over HZSM-5 zeolite catalysts

P. Lestinsky*, K. Klemencova, B. Grycova, A. Inayat

Institute of Environmental Technology, CEET, VSB-TUO, Ostrava, Czech Republic
**pavel.lestinsky@vsb.cz*

Keywords: zeolite, catalyst, catalytic cracking, aromatization

Introduction. Now a days, due to ever stricter environmental regulations on CO_2 emissions, alternative routes (other than involving coal and crude oil) for BTEX production are attracting the attention of researchers. At the same time, we are dealing with the problem of waste plastics, particularly polyolefins, a solution presents itself - aromatization of hydrocarbons from pyrolysis of waste polyolefins [1]. During the pyrolysis of waste polyolefins, a wide spectrum of gaseous (C_1-C_4) and liquid hydrocarbons (C_5-C_{20}) is produced. These compounds subsequently undergo aromatization over suitable catalysts. In this regard, in order to improve the aromatic yield and selectivity during catalytic treatment of waste polyolefins, it is important to gain enhanced understanding of cracking and the following aromatization processes. Therefore, the aim of the present work is to study cracking and aromatization of the most common hydrocarbons individually, which are produced as intermediates during the thermo-catalytic treatment of waste polyolefins.

Experimental/methodology. As feedstocks, both saturated (C_5-C_{12}: including straight, branched and cyclic) and unsaturated liquid aliphatic hydrocarbons were employed. As catalyst materials, HZSM-5 zeolites featuring different silica to alumina ratios and, consequently, having different acid site densities were used. The liquid hydrocarbons were continuously fed to the evaporation chamber and the resulting vapors were passed over a fixed bed of HZSM-5 zeolite catalyst at 500 °C. The products were passed through a cooling unit to separate liquid and gaseous fractions, which were then analyzed by GC-FID/TCE and GC-MS systems.

Results and discussion. The results obtained from preliminary tests showed that the liquid aliphatic hydrocarbons underwent both cracking and aromatization. Furthermore, it was observed that the chain length and type (straight, branched or cyclic) influenced both conversion and aromatization significantly. Moreover, in the case of branched chain hydrocarbons, no aromatization was detected, which can be attributed to their increased molecular size as compared to straight chain hydrocarbons of the same carbon number/molecular weight. For the conversion of such compounds, zeolites with additional mesoporosity might be interesting catalytic materials. A detailed and systematic study on the conversion of abovementioned hydrocarbons to aromatics over HZSM-5 zeolite catalysts will be presented.

Acknowledgments
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Light olefins production with high and flexible selectivity by catalysis integrated electrified process

YN.Kim, CM.Jung and DH.Lee *

[1] *Korea Institute of Machinery and Materials, 156 Gajeongbuk-Ro Yuseong-Gu, Daejeon, Republic of Korea*
**dhlee@kimm.re.kr*

Keywords: Light olefins, arc plasma, plasma chemical process

Introduction.

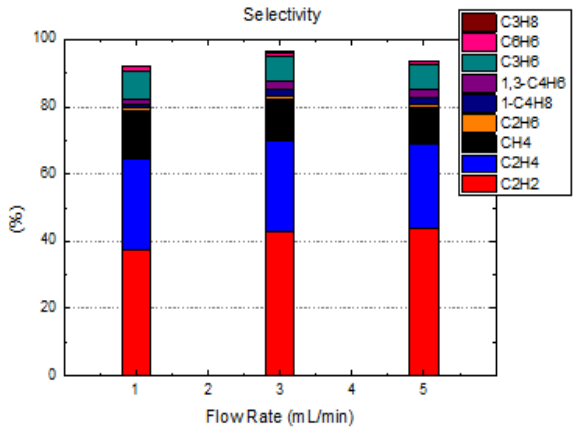
Light olefins are significant raw materials in downstream chemical industry. Main process for light olefin production is thermal cracking of hydrocarbons such as light naphtha in the presence of steam. The thermal cracking process is the most energy intensive process in petrochemical industry and cause high amount of CO_2 emission. However, this half of century used industrial process is being asked to change due to the recent climate change and strong demand for CO_2 emission suppression. Here, we demonstrated an environmentally benign way for the light olefin production by using plasma. The plasma process can provide enough thermal conditions for conversion of feedstock to light olefin from renewable electricity. Also, several kinds of different compound having same carbon number were compared as feedstock for olefin production in order to reveal the effects of molecular structure. In results, this work shows that electrified plasma process can produce highly selective light olefins having flexible range depending on operation conditions and molecular structures.

Experimental/methodology.

The mixed gases for plasma discharge and the reaction are injected to the reactor having swirl flow. The feed for the olefin production is injected by syringe pump as a liquid phase. The converted products are pass through catalysis part. The feed and product gases are analysed by online GC-MS(5975C model, Agilent 19091P-K33 column, Agilent Technologies) and microGC(990 Micro GC, MS5A SS and PoraPLOT U FS columns, Agilent Technologies) using sample bag.

Results and discussion.

The figure shows the selecitivty of C_1-C_4 products under different flow rate of liquid hydrocarbons as feed.



The selectivity was calculated as following equations.

$$Selectivity_{C_xH_y}(\%) = \frac{x \times moles\ of\ C_xH_y\ produced}{6 \times moles\ of\ C_6\ converted} \times 100$$

In this graph, the ethylene selectivity is range from 20 – 30% depending on the flow rate conditions. Especially, the selectivity of propylene is alomost 10%. In results, more than 30% selectivity of C_2-C_4 olefin are produced. Moreover, ethylene selectivity can be increased about 40% by simple cataytic hydrogenation process of acetylene. As considerd light olefin selecitivty (C_1-C_4) of conventional thermal cracking process and previous researches, this potential selectivity for light olefins is extraordinary.

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Turquoise H2 and Carbon production through CH4 Cracking

A. Batistini[1], V. Cosentino[1*], G. Iaquaniello[1], E. Palo[1], B. De Caprariis[2], P. De Filippis[2]

[1]*NextChem Spa, Via di Vannina 88/94, 00156 Rome, Italy*
[2]*Department of Chemical Engineering, University La Sapienza di Roma, Via Eudossiana 18, 00184 Rome, Italy*
[*]*v.cosentino@nextchem.it*

Keywords: turquoise hydrogen; methane cracking; carbon; molten metal process; CO2 free process

Introduction. Up to 80% of hydrogen production is currently carried out through CO2 emission-intensive processes. The two main low-carbon production routes are Steam Methane Reforming coupled with CCUS (blue H2) and water electrolysis (green H2) [1]. NextChem has developed a new competitive process scheme based on methane cracking (turquoise H2) (Fig.1) [2], based on the use of a molten metal bubble reactor where the reaction, which leads to the production of only H2 and solid carbon without CO2 emissions, occurs. Experimental tests were carried out at the Industrial Chemistry laboratory, Department of Chemical Engineering University of La Sapienza in Rome [3]. From experimental tests, it was possible to obtain the data for the overall process scheme. A mathematical model was developped to predict CH4 conversion, solved for both lab-scale and industrial-scale reactors [3]. A techno-economic assessment of the industrial thermal cracking process was carried out for a capacity of 5'000Nm3/h of H2 (Fig.1).

Experimental/methodology. A tubular fixed-bed quartz reactor of different diameters was tested with a molten metal height up to 20cm. The reactor was heated by an electric furnace varying the temperature between 950°C-1070°C. The temperature was controlled by a K-type thermocouple. CH4 flow rate could be varied in a range 30-140ml/min. Differents molten metals (tin and tin alloys) were tested to evaluate both thermal and catalytic cracking.

Results and discussion. The main results, reported in Fig.2 for a CH4 flow rate of 45ml/min, show an almost equal behavior between pure Sn and the first Sn/Sb/Cu alloy in the whole temperature range. It seems that Sb and Cu do not have a catalytic behaviur on the system. Further experimental campaigns are on going with other percenatage of these elements and/or other alloys. The carbon structure, on the other hand, is affected by the presence of different metals, presenting a ordered structure in the case of Sn/Sb/Cu. Data for pure Sn were used to validate the developed mathematical model with a quite accurate final fit [3]. For the economic analysis, NextChem's innovative solution demonstrates a levelized cost of hydrogen (LCOH) of 1.75€/kg of H2 with a total energy consumption of about 1.2kWh/Nm3 of H2, proving to be competitive with benchmark solutions. It can be concluded that Methane Cracking on molten media represents a promising process for low-emission Hydrogen production.

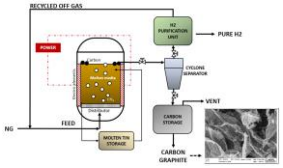

Fig.1: NextChem methane cracking process scheme [2]

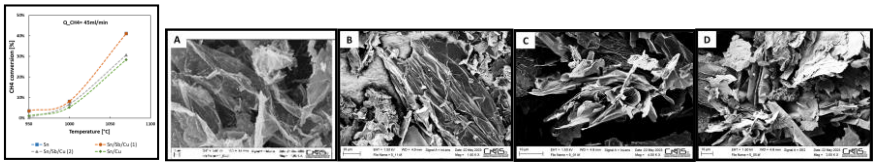

Fig.2: CH4 conversion [%] vs. T [°C] with different molten metal and correspective carbon structure (A tin, B/C/D alloy)

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Surface science & atomic level models: experiment and theory

Real-time observation of catalytic hydrogen oxidation by *in situ* correlative surface microscopy

Philipp Winkler, Johannes Zeininger, Maximilian Raab, Yuri Suchorski, Günther Rupprechter*
Institute of Materials Chemistry, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria
**guenther.rupprechter@tuwien.ac.at*

Keywords: photoemission electron microscopy, field emission microscopy, rhodium, hydrogen oxidation, reaction fronts, oscillations, single particle catalysis.

Introduction. Nanostructured metals are important functional materials for energy-relevant catalytic reactions. The oxidation of hydrogen to water by solid catalysts enables energy generation without combustion and without pollution, e.g., in fuel cells. For future developments of new green energy production technologies, it is important to monitor ongoing catalytic reactions by *in situ* microscopy of working catalyst surfaces. Two examples are presented, covering meso-scale planar Rhodium surfaces and a single Rh nanoparticle (*single particle catalysis*).

Experimental/methodology. Several different microscopic techniques (see below) were combined for *in situ* imaging of catalytic H_2 oxidation on the same structures of the same Rh sample, i.e., in a *correlative* approach preferentially operated in a single setup under truly identical reaction conditions.

Results and discussion. i) Using a correlative microscopy approach [1,2], H_2 oxidation on polycrystalline Rh foil was studied by scanning photoelectron microscopy (SPEM) and photoemission electron microscopy (PEEM), which allow local surface analysis and visualising the heterogeneity of ongoing reactions on a µm-scale. This revealed an anisotropy of surface oxidation, yielding an oxidation map, as well as the reaction mechanism involving subsurface oxygen. *In situ* PEEM imaging of ongoing H_2 oxidation directly compares the local reactivity of metallic and oxidised Rh, revealing a high transient activity of Rh surface oxide. Higher spatial resolution and chemical sensitivity were provided by low energy electron microscopy (LEEM) and XPEEM, revealing a new front propagation mechanism.

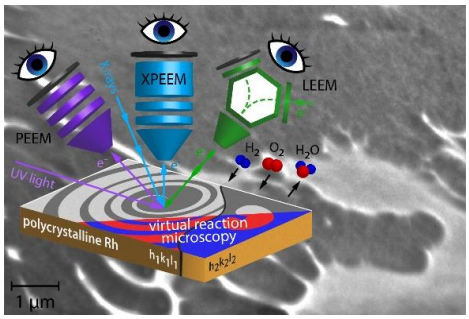

Figure 1. Concept of correlative microscopy and LEEM image of hydrogen oxidation on Rhodium [1].

ii) Using the apex of a Rh-nanotip as model structure, *single particle catalysis* [3,4] was studied on the nm-scale by field emission microscopy (FEM) as imaging tool. Novel effects were revealed, such as nanoscale multifrequential oscillations and limited interfacet coupling. Using ionized water as imaging species, the active sites on the metal nanotip were directly imaged by field ion microscopy (FIM).

The obtained insights may stimulate new ways of metal catalyst design and operation.

Acknowledgments
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Computed Surface Phase Diagram for Hydrogen on Pd Surfaces

Igor Kowalec,[1] Herzain I. Rivera-Arrieta,[2] Andrew Logsdail,[1] C. Richard A. Catlow,[1,3] Matthias Scheffler[2] and David J. Willock[1]*

[1] *FUNCAT, Cardiff Catalysis Institute, Cardiff University, Park Place, Cardiff, CF10 3AT, UK.*

[2] *The NOMAD Laboratory at the Fritz-Haber-Institut der Max-Planck-Gesellschaft and IRIS Adlershof of the Humboldt-Universität zu Berlin, Germany.*

[3] *Department of Chemistry, University College London, 20 Gordon St., London, WC1 HOAJ, UK.*

[*] *willockdj@cardiff.ac.uk*

Introduction.

Pd based heterogeneous catalysts are used in a range of hydrogenation reactions.[1] In these reactions the surface of Pd will move from pure metal to full hydride as the hydrogen partial pressure is increased at a given temperature. As the level of hydrogen coverage will affect the reactivity of the surface, computer modelling should use an appropriate surface coverage when calculating the potential energy surface for hydrogenation reactions. In this contribution we use an *ab initio* thermodynamics approach to calculate an effective phase diagram for hydrogen adsorbed to Pd(111) and Pd(100) surfaces.

Experimental/methodology.

The energy of configurations was calculated using the full potential all-electron periodic DFT code, Fritz Haber Institute *ab initio* materials simulations (FHI-aims) package, with functionals linked from the LibXC density functional library. Calculations were controlled and analysed usingfunctionality of the Atomic Simulation Environment (ASE). The meta-generalised gradient approximation (MGGA) semi-local Bayesian error estimation (mBEEF) exchange-correlation functional is employed throughout this work.

For surface calculations, *p*(3×3) supercell slab models for Pd(111) and Pd(100) consisting of 5 atomic layers were constructed. During geometry optimisations the top 4 (Pd(111)) and top 3 (Pd100) layers are unconstrained. H atoms are added to the top most surface of the slabs interacting with unconstrained Pd atoms. Geometry optimisations were performed using a force convergence criterion of 1×10^{-2} eV Å^{-1}.

Results and discussion.

Both slab models are supercells with 9 atoms in the surface layer. For one H atom the fcc and hcp hollow sites on Pd(111) and the hollow and bridge sites on Pd(100) have significantly lower calculated adsorption energies than any alternatives. To generate higher surface coverages H atoms are placed on the surface in these sites. The number of possible configurations rapidly increases up to 1 ML (9 H atoms) with 48,620 possibilities at 1 ML on Pd(111). A full set of calculations of all configurations up to 2 ML on Pd(111) would require 262,143 structural optimisations.

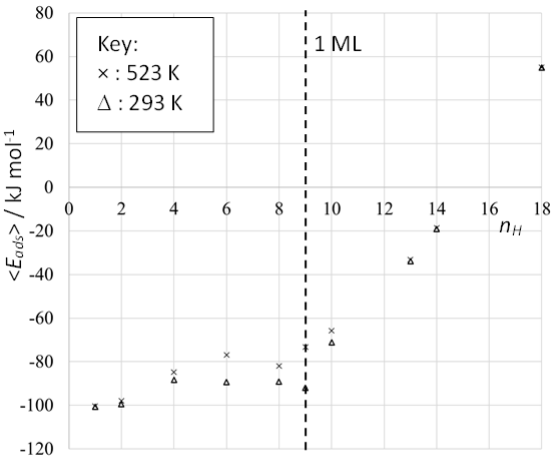

Figure 1: <E_{ads}> for H_2 adsorbed on Pd(111) *vs* num. H atoms, n_H. Temperatures in the key. 1 ML : 1 monolayer.

However, since the slab models are produced from supercell expansions of the primitive cell there is underlying symmetry. We have developed an algorithm to enumerate all configurations and identify the symmetry related configurations with the associated degeneracy. This makes direct DFT calculation of the configuration averaged adsorption energy tractable resulting in the temperature dependent averaged adsorption energy behaviour shown in Figure 1.

This data can be used to calculate the phase diagram for the Pd surfaces exposed to hydrogen at a range of partial pressures and temperatures and enables us to identify the conditions under which hydride formation with sub-surface hydrogen becomes significant.

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Rapid Hydrogen Mobility over Ru Nanoparticle-Doped Polar MgO(111) Surface

T. Yoskamtorn[1], J. Mo[1], L. Chen[2], S. Wu[1], S. Mukhopadhyay[3], A. Hawkins[3], X.-P. Wu[2*], S. C. E. Tsang[1*]

[1]Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford, OX1 3QR, U.K.
[2]Key Laboratory for Advanced Materials, Centre for Computational Chemistry and Research Institute of Industrial Catalysis, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P.R. China
[3]ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Didcot OX11 0QX, U.K.
**edman.tsang@chem.ox.ac.uk*

Keywords: hydrogen diffusion, quasielastic neutron scattering, hydrogen capture, polar oxide surface, nanocatalyst

Introduction. Diffusion of hydrogen (H) on solid surfaces, such as metal oxides, at elevated temperature under gas phase hydrogen (H_2) plays a key role in a broad range of chemical processes, especially in energy storage, fuel cells, and catalysis. However, the dynamics of the H migration over the catalyst surfaces still remain unclear and extremely difficult to observe experimentally on atomic length scales. Thus, it is of importance to probe the diffusion of H over the catalyst surface using high-resolution equipment having the ability to detect the dynamics of such a light element under realistic conditions. Here, A key strength of quasielastic neutron scattering (QENS) is its extreme sensitivity to H motions due to a significantly larger incoherent cross-section of the H atom (80.26 barns, where 1 barn = 10^{-24} cm^2) compared to all other scattering cross-sections. This renders QENS to be one of the most powerful tools to study diffusion in which H is involved.

Experimental/methodology. Metal oxide-based materials including Ru/MgO(111) and Ru/MgO(110) investigated in this study were prepared by following the procedure previously reported by our group [1,2]. In situ QENS technique was used to study the H mobility on the Ru-based MgO catalyst surface, as a function of temperature and H_2 pressure. The QENS experiments were performed on the OSIRIS instrument, a high-flux backscattering, TOF spectrometer with an inverted geometry at the ISIS Pulsed Neutron and Muon Source, Rutherford Appleton Laboratory. Details of the in situ QENS experiments are given in [3].

Results and discussion. QENS results reveal an exceptional diffusion rate on the polar facet via a proton (H^+) hopping mechanism. The observable H^+ hopping occurs across the surface oxides (O^{2-}) of the MgO(111), with an average jump distance nearly equivalent to the distance between oxide anion sites. This degree of H^+ mobility is drastically less detectable when using the Ru/MgO(110) material, suggesting a key role of polar metal oxide surface in facilitating the fast H^+ transport. The H^+ diffusion coefficients are in between 1.41 ± 0.25 and 2.46 ± 0.72 × 10^{-5} cm^2 s^{-1} under the temperature of 573–623 K and the H_2 pressure range of 1.0–5.0 bar. These values outperform those of H^+-conducting oxides, reaching to a similar magnitude to oxyhydride materials. The calculated activation energy for this H^+ hopping is ≈0.3 eV, also sensibly lower than H^+-conducting oxides in which H^+ is covalently bound to local O^{2-} sites. This observation is attributed to the unique atomic arrangement of alternate layers of Mg cations and O anions of the polar MgO(111) where the strong electrostatic field of terminal oxygen anions facilitates protonic migration with a lower degree of local covalency. We envisage that this finding of using polar oxide facets will provide insights into the rational design of efficient catalysts for H diffusion-involved reactions.

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In situ NAP-XPS characterization of PdAg single crystals and polycrystalline thin films

Ingeborg-Helene Svenum[1,2], Marie D. Strømsheim[2,3], Jan Knudsen[4,5], Mehdi Mahmoodinia[2], Andrey Shavorskiy[5], Junbo Yu[2], Virgínia Boix[4], Thijs Peters[1], Hilde J. Venvik[2,6]

[1]*SINTEF Industry, Trondheim and Oslo, Norway*
[2]*Dept. Chem. Eng., NTNU - Norwegian University of Science and Technology, Trondheim, Norway*
[3]*Hydrogen Mem-tech AS, Trondheim, Norway*
[4]*Division of Synchrotron Radiation Research, Department of Physics, Lund University, Sweden*
[5]*MAX IV Laboratory, Lund University, Sweden*
[6]*Dept. of Chemical Engineering, Faculty of Engineering, Lund University, Sweden*

Keywords: palladium, silver, single crystal, CO oxidation, hydrogen absorption, segregation, surface oxide

Introduction. *In situ* near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) can elucidate the dynamics between segregation, surface or bulk oxide formation, and adsorption during reaction. We have compared $Pd_{75\%}Ag_{25\%}$ (100) [1] and (111) [2] single crystals to their pure Pd counterparts, with CO oxidation in excess oxygen as the test reaction. But ultrathin PdAg alloy membranes are also being commercialized for production of H_2 from natural gas with CO_2 capture and storage. We therefore study the adsorption, reactivity, and segregation of Pd-23wt%Ag polycrystalline films *in situ* under hydrogen permeation [3].

Experimental/methodology. A combination of in-house characterization and performance testing and near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) at the MAXIV HIPPIE Beamline (Proposals 20180307, 20190540, 20190949) has been used. CO oxidation was studied at ~2 mbar and O_2/CO=10 during temperature cycling (up to 600 °C). Hydrogen adsorption-permeation was studied *in situ* at 1-5 mbar H_2 in a permeation cell designed for polycrystalline thin metal films, with comparison to ambient pressure exposures in permeation experiments without and with (up to 10%) CO or CO_2 present.

Results and discussion. Alloying significantly affects the reactivity of $Pd_{75\%}Ag_{25\%}$ relative to pure Pd (Fig. 1a) [1,2]. The segregation dynamics responds to exposure and temperature changes and can be followed through the relative amount of Pd bound to CO as well as the ($3d_{5/2}$) Pd/(Pd+Ag) ratio. The CO_2 formation is much lower on $Pd_{75\%}Ag_{25\%}$ (111) than on Pd(111) and there are no hysteresis effects. XPS confirms gas phase CO present near the surface, i.e., the commonly observed mass transfer limitations are circumvented by moderation of Pd(111) with Ag. In contrast to Pd(111), and albeit the (√6x√6) Pd_5O_4 surface oxide also forming on $Pd_{75\%}Ag_{25\%}$ (111) under pure O_2, this surface oxide is immediately lifted upon changing to O_2:CO=10 at 450 °C (Fig 1b). The impact of alloying also depends on the surface termination and is stronger for (111) than for (100) [2]. Segregation dynamics is also observed for the Pd-23wt%Ag polycrystalline thin films by NAP-XPS during hydrogen adsorption and dissolution [3].

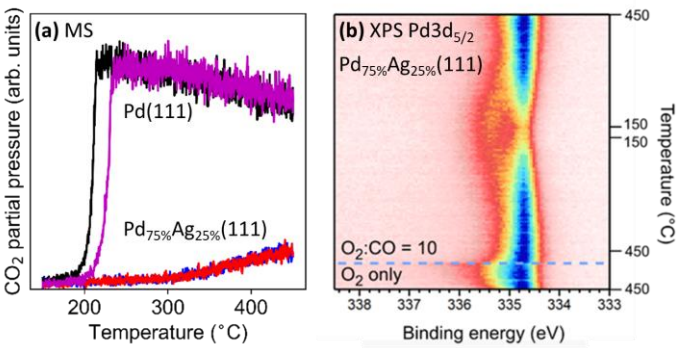

Figure 1: (a) CO_2 formation mass spectrometry profiles for Pd(111) and $Pd_{75\%}Ag_{25\%}$(111) and (b) $Pd3d_{5/2}$ live spectra during initial surface oxidation followed by temperature cycling during CO oxidation for $Pd_{75\%}Ag_{25\%}$(111).

Acknowledgments
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Atomic Charges and a 10-Electron Count Rule To Predict the Reactivity of Single-Atom Alloy Catalysts

R. Réocreux[1,2]*, J. Schumann[1,2], A. Michaelides[2], M. Stamatakis[1]

[1]*Thomas Young Centre and Department of Chemical Engineering, University College London, Roberts Building, Torrington Place, London WC1E 7JE, UK*
[2]*Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, CB2 1EW Cambridge, UK*
*r.reocreux@ucl.ac.uk

Keywords: single-atom alloys, DFT, orbitals, atomic charges

Introduction. Embedding single atoms of transition metals into the surface of coinage metals (Cu, Ag and Au) has emerged as an effective atom-efficient approach to create active and selective catalysts. These so-called Single-Atom Alloys (SAAs) have proven to perform chemistries deemed as unattainable with pure transition metal catalysts [1]. This unique behaviour results from the SAAs' ability to escape decades-old models (d-band model, scaling relationships) that have successfully predicted the reactivity of more traditional metal catalysts [1]. With no predictive models, however, the design of new SAA catalysts is confined to trial-and-error approaches. Here we show that atomic charges and electron count rules are better suited for the identification of potentially active SAA catalysts.

Experimental/methodology. All Density Functional Theory (DFT) calculations have been performed using the optB86b-vdW functional and the Vienna *Ab Initio Simulation Package*. Further electronic analyses (orbital projection, overlap analyses) have been performed using the LOBSTER code (http://www.cohp.de).

Results and discussion.

To identify potential electronic descriptors for the reactivity of SAAs, two high throughput campaigns have been designed [2-3].

Following the (yet-scarce) experimental evidence of the existence of localised electrostatic charges on the dopant of SAAs [1], we have first determined the dopant charges of Cu, Ag and Au surfaces doped with Rh, Ni, Pd and Pt. Computed dopant charges show large differences among SAAs (-0.63e on PtCu vs +0.32e on NiAu) and could play a role in the binding of adsorbates [2]. To test this hypothesis, we have computed the binding energies of a large range of catalytically relevant adsorbates (H, CO, CH_x, OH_y, NH_z, CH_3OH). We have shown that the binding energies correlate with the dopant charges for a subset of adsorbates, namely electron rich Lewis bases such as H_2O, OH, and NH_3, suggesting that the binding energy can be decomposed into an electrostatic contribution (dominating in this subset) and a covalent contribution. By linearly combining the dopant charge (descriptor of the electrostatic term) and the binding energy for carbon (proxy for the covalent term), we reproduce the DFT data within 0.06 eV mean absolute error and 0.07 eV standard deviation. We also propose an adsorbate classification based on the relative importance of the two identified terms.

Although this classification already provides a very intuitive theoretical framework for the rationalisation of reactivity trends on SAA catalysts, the covalency descriptor only gives indirect information about the dopants and ignores their electronic structure [3]. In our attempt to identify an electronic descriptor for the covalent contribution, we have extended our high throughput approach to most of the d-block elements as potential dopants (3d, 4d and 5d). The obtained periodic trends reveal that the optimal binding energy is reached when the total number of valence electrons of both the dopant and the adsorbate reach 10. Further electronic structure analyses show that this corresponds to the saturation of the d-orbitals of the dopant. Finally, we illustrate how this 10-electron count rule can be used for the identification of promising SAA catalysts (in particular Mo, W and Re based SAAs) for the reduction of nitrogen to ammonia, a reaction of industrial significance.

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Thermodynamic and kinetic impacts of chlorine on Platinum single atoms supported on γ–Al_2O_3 during calcination and reduction

A. Hellier[1*], C. Chizallet[1], P. Raybaud[1,2]

[1]*IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, 69360 Solaize, France*
[2]*ENS Lyon, CNRS, Laboratoire de Chimie UMR 5182, 46 Allée d'Italie, 69364 Lyon, France*
[*]*adrien.hellier@ifpen.fr*

Introduction. Platinum based catalysts supported on γ-Al_2O_3 are used in a great variety of industrial chemical processes, including refining and biomass conversion. The activation steps (calcination and reduction) of these catalysts involve the transformation of oxidized platinum single atom (Pt SA) complexes into the reduced active phase containing both Pt clusters and Pt SA (Fig. 1.a))[1]. However, the exact nature of these intermediate species and the mechanisms of their transformation during activation remain unknown. By density functional theory (DFT) calculations, we propose to decipher the thermodynamic and kinetic features of these activation steps, and demonstrate the crucial role of chlorine on the mechanisms linking Pt^{IV}, Pt^{II} and Pt^0 species, as well as on their mobility.

Experimental/methodology. DFT calculations have been carried out by using the PBE-dDsC and HSE06 functionals when needed[2] as implemented in VASP 5.4.1. Transition states and free activation energies were determined with the CI-NEB, Dimer method, intrinsic reaction coordinate and vibrational calculations. All supported complexes were modelled on the γ-Al_2O_3 (100) surface.

Results and discussion. During calcination, chlorine induces a strong dependence between the coordinative shell of Pt and the operating conditions. At high temperature (>500 K), PtO_2, $PtOCl_2$ (tetrahedral) and $PtCl_4$ (pentahedral) are predicted to exist, depending on P(HCl), used as a descriptor of the amount of chlorine in the system. At lower temperature, octahedral $PtCl_x(OH)_{4-x}(H_2O)$ species are expected. Our models were fruitfully compared to XAS experiments, in particular in terms of coordination numbers and Pt-X (X=O or Cl) bond lenghts. For reduction, we predict that chlorine increases the thermodynamic stability of Pt^{II} species such as $PtCl_2$ by increasing the reduction temperature and by decreasing its affinity for H_2. Moreover, from a kinetic point of view, chlorine hardens Pt reduction by increasing the activation barrier up to 174 kJ/mol for $PtCl_2 \rightarrow Pt$ against 148 kJ/mol for $Pt(OH)_2 \rightarrow Pt$ (Fig. 1.b)). In addition, Cl also favours the migration of $PtCl_2$ (barriers of 14 kJ/mol) onto an alumina surface site where it cannot be reduced (Fig. 1.b)). $Pt(OH)_2$, conversely, is reluctant to migration (barriers of 144 kJ/mol) due to strong Pt-(OH)-Al bridges. This result might explain the higher proportion of SA observed experimentally in presence of chlorine[1] (Fig. 1.a)). Our study paves the way to a better control of the properties of Pt/γ-Al_2O_3 catalysts by tuning activation conditions.

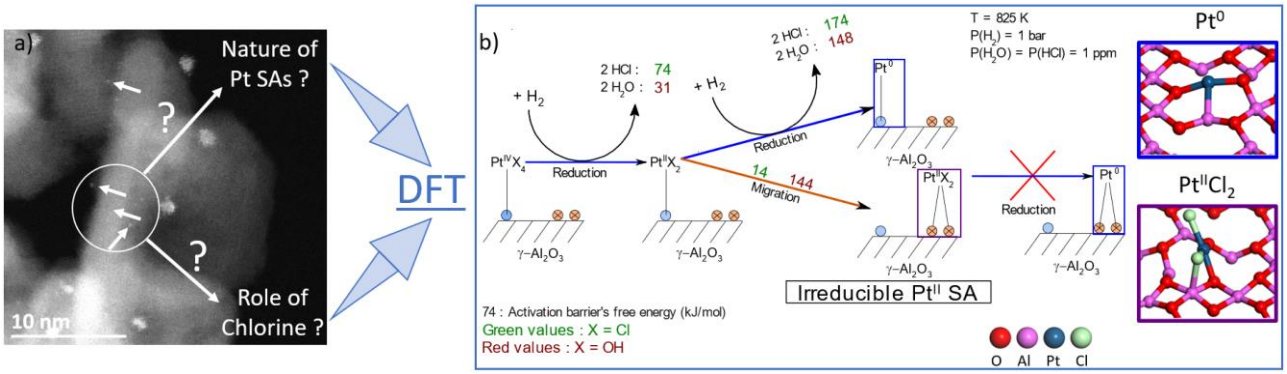

Figure 1. a) HR-HAADF-STEM images of a reduced Pt/γ–Al_2O_3 catalyst [1]. White arrows exhibit Pt SAs. b) DFT scheme of the chlorine impact on the kinetics of platinum reduction and atomistic models of SA Pt/γ–Al_2O_3.

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Computational Identification of True Active Sites in Electrocatalysis

Matthias Vandichel*
Matthias.Vandichel@ul.ie
Department of Chemical Sciences and Bernal Institute, University of Limerick, Ireland

Keywords: Electrocatalysis, DFT, OER, HER

Introduction. The transition of society to energy sustainability necessitates the production of fuels and chemicals via new renewable energy technologies such as electrolyzers. The development and understanding of cheap, durable and high-performance electrocatalyst systems will be necessary to reach sustainable development goals. Future hydrogen production from excess renewable power will rely on superior electrocatalysts for the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) taking place at anode and cathode, respectively. In this talk, recent computational results for various OER and HER catalysts and supporting experimental observations will be discussed.[1-12]

Experimental/methodology. Density functional Theory (DFT) calculations were performed with the Vienna Ab initio Simulation Package (VASP) and compared with experimental data.

Results and discussion. To identify what drives an electrocatalytic process, the true active sites need to be identified and molecular modelling can help to identify the dominant reaction pathways on various molecular model systems and assess their electrochemical stability. In case of OER, the usage of electrolyte solutions (*e.g.* KOH) containing trace amounts of Fe and Ni, can result in the creation of active material interfaces under relevant anode conditions, which cheap oxygen evolution catalysts at alkaline pH. Computationally, mixed (Fe, Ni, Co) metaloxy-hydroxides are stable under OER conditions, and their excellent OER-activity can be proven assuming a bifunctional mechanism.[1-2] In this regard, the beneficial effect of Fe-doping of other oxides (PdO_x, MnO_x) will also be discussed.[3-4] Furthermore, molecular metal-complexes are merely OER-'pre'catalysts, and case examples will be presented that point towards their decomposition;[5-7] for a vitamin B12 complex electrochemical leaching of Co is more likely to happen than the oxygen evolution reaction.[6-7] In case of HER, the hydrogen adsorption energy – typically used as activity descriptor – is determined to identify active sites.[8-9] We showed that carbon sites on a nanotube containing PtRh are more active for the hydrogen evolution reaction than other possible model systems,[8] and that cathodic hydrogen absorption results in metal-hydride formation, which changes the activity through strain and coordination.[9] Besides typical HER and OER process, I will present modelling results of various photo(electro)chemical processes taking place on material interfaces [11-12] and work in progress.[13] Summarizing, it should be clear that first-principles insights can transcend the viewpoint of the scientific community beyond the state-of-the-art and contribute to an enhanced understanding.

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Unrevealing Universal Water-Assisted Chemical Routes Towards the Oxygen Evolution Reaction at solid-liquid interfaces

F. Creazzo[1*], R. Ketkaew[1], S. Luber[1]

[1]*University of Zurich, Zurich, Switzerland*
[*]*fabrizio.creazzo@chem.uzh.ch*

Introduction. The biggest (or one of the biggest) issue that the world human population faces in this century is the urgent need for clean and renewable technologies. Herein, advanced enhanced sampling methods coupled with spin-polarized Density Functional Theory Molecular Dynamics (DFT-MD) simulations, which include in a realistic way finite-temperature and explicit-solvent effects, are applied to gain a global understanding of (100) RuO_2, (001) WO_3, (100) WSe_2 aqueous interfaces in catalyzing the Oxygen Evolution Reaction (OER), and hence possibly help in the design of novel catalysts in the context of photochemical water oxidation. Notwithstanding (100) RuO_2, (001) WO_3, (100) WSe_2 are gaining attention for active catalysts toward OER, a plethora of fundamental details on their catalytic properties are still elusive as well as the water interfacial organization, severely limiting their large-scale deployment.

Experimental/methodology. An atomistic understanding of structural, electronic and mechanical properties of bulk RuO_2, WO_3 and WSe_2 and explicit solvent effects on (110)-RuO_2, (001) WO_3, (100) WSe_2 facets are provided in the context of (photo)electrochemical conditions. We focus on the comprehension of the mechanistic interplay between surface wettability, interfacial water dynamics and surface chemical activity. Moreover, we provide a dependence of physical and chemical properties, such as surface electric field and work function in-and-out the presence of interfacial water with different degrees of surface wettability [1,2].

Results and discussion. Furthermore, we quantitatively assess the kinetics, thermodynamics and the involved energies behind the OER at (100) RuO_2, (001) WO_3, (100) WSe_2 catalyst surfaces revealing plausible pathways composing the reaction network of the O_2 evolution in both gas-phase and explicit solvent model [3,4]. Albeit a unique efficient pathway has been identified in the gas-phase OER, a lower-energy-requiring reaction route can be possible when facets are in contact with liquid water.

By estimating the free-energy surfaces associated to these processes, we reveal an unprecedented and universal water-assisted OER mechanism which involves a crucial proton-transfer-step assisted by the local water environment. These findings pave the way toward the systematic usage of those techniques for the fine assessment of the activity of catalysts.

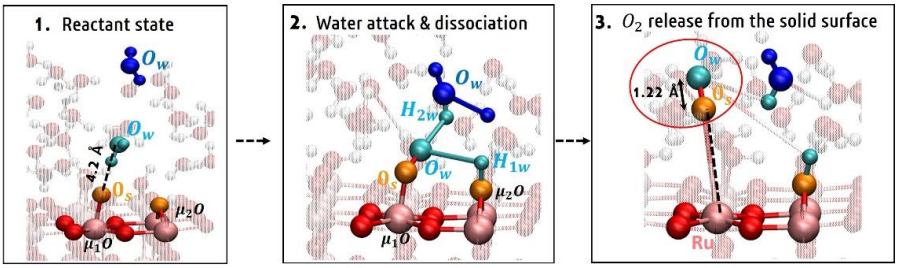

Fig. Water-assisted OER mechanism at the (110)-RuO_2 facet in explicit solvent model.

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Towards more realistic simulations of catalysis: supported metal nanoclusters on oxide surfaces

E. Strugovshchikov,[1*] A. Salom-Català,[1] J. Pan,[1] K. Kaźmierczak,[2] D. Curulla-Ferre,[2] J.J. Carbó[1] and J.M. Ricart[1]

[1] *Universitat Rovira i Virgili, Departament de Química Física i Inorgànica, Tarragona, Spain*
[2]*TotalEnergies OneTech Belgium, Feluy, Belgium*
[*]*evgenii.strugovshchikov@fundacio.urv.cat*

Supported sub-nanometric metal clusters are considered as a singular phase of matter exhibiting a number of interesting properties that can be used in the design and development of novel catalytic materials. For instance, metal sites on an oxide surface can exhibit high activity combined with enhanced selectivity, and decreased deactivation by undesired products.[1] However, their atomistic simulation requires the consideration of a complex variety of the possible active sites at the sub-nanometric level as well as the large number of the accessible atomic configurations at reaction temperatures.

The study of such a catalytic system, which is not easily accessible using Density Functional Theory, can be performed by implementing specific Reactive Force Fields capable of performing extensive simulations or identifying descriptors for the structure-activity relationship. Thus, we have adopted the ReaxFF method,[2,3] which employs the so-called bond order formalism, and is able to simulate bond formation/breakeage processes in systems of similar size to classical Molecular Dynamics simulations.

As a case study, we present a theoretical simulation of alumina-supported (γ-Al_2O_3) Pt and Pt-Sn sub-nanometric clusters for propane dehydrogenation (PDH) reaction.[4,5] To this end, we have developed a set of new parameters for the ReaxFF reactive force field. We will demonstrate that these ReaxFF parameters are capable to describe not only the productive PDH pathway but also deactivation routes involving deep dehydrogenation and C-C bond scission. Furthermore, our theoretical approach opens the way for the more efficient ensemble representation of nanocatalysts, bridging the gap between atomic-scale modelling and mesoscale experimental techniques, thus offering a possibility to design a more effective catalyst.

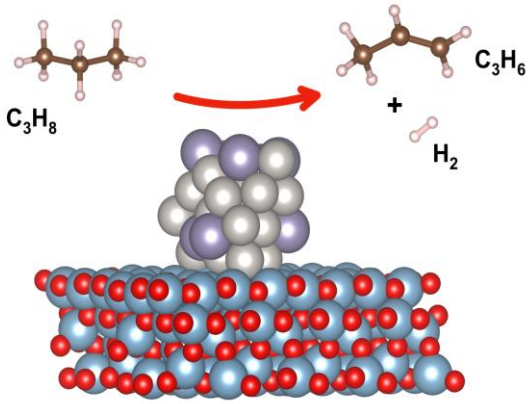

Figure 1. Pictorial representation of PtSn sub-nanometric clusters on γ-Al_2O_3, and propane dehydrogenation to hydrogen and propene. Pt – grey, Sn – violet, Al – blue, O – red, C – brown, H – whitish.

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Innate dynamics of a metal surface unveiled by machine learning of atomic environments

M. Cioni[1], D. Polino[2], D. Rapetti[1], L. Pesce[2], M. Delle Piane[1], G.M. Pavan[1,2*]

[1]*Department of Applied Science and Technology, Politecnico di Torino, 10129 Torino (Italy)*
[2]*Department of Innovative Technologies, University of Applied Sciences and Arts of Southern Switzerland, 6962 Lugano-Viganello, (Switzerland)*
[*]*giovanni.pavan@polito.it*

Introduction

Solid's surfaces are known to become mobile due to thermal energy at temperatures well below the melting point. As pointed out by Spencer[1], many metals used in industrial catalytic processes work above the Hüttig temperature ($T_{Hüttig} \approx 1/3\ T_{melting}$), thus their surfaces should be mobile. Understanding how such surfaces move and reconstruct may be essential to determine their activity[2] e.g., establishing the number of active sites and their evolution in time. In this work we focused on copper (Cu) due to its relevance in several fields of catalysis such as methanol synthesis from CO_2[3]. An extensive campaign of DFT molecular dynamics (MD) simulations generated Cu surface data used to train a deep neural-network (NN) potential. This provided a dynamically accurate atomistic force field allowing to simulate various types of Cu FCC crystal facets above $T_{Hüttig}$ on relevant spatiotemporal scales. Smooth Overlap of Atomic Position (SOAP)[4] based analyses revealed the atomic environments that statistically populate Cu surfaces, including atomic environments typical of other types of Cu surfaces, which continuously emerge/resorb in equilibrium conditions. This allows estimating an "equivalent identity" for such metal surfaces on a statistical basis from the data emerging along the simulations.

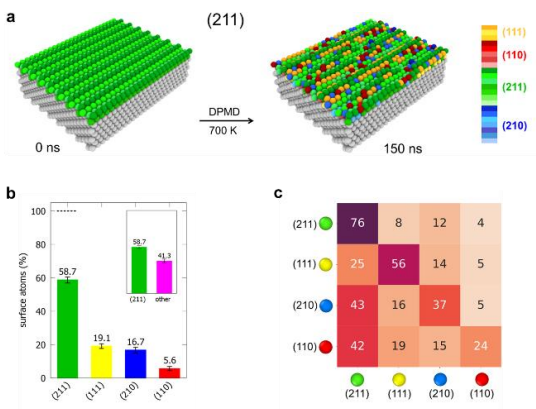
Methodology

A Cu NN-potential was built following the Deep Potential MD scheme[5]. The training data set was obtained from ab initio MD simulations of small Cu surfaces and bulk structures carried out in the NVT ensemble at 500-700 K. MD simulation of larger systems were performed and analyzed with the local environment descriptor SOAP. Environment similarity analyses were performed to characterize the atomic environments that statistically populate metal surfaces in equilibrium conditions. We created a dictionary of SOAP atomic environments by computing the SOAP spectra for all atoms in the optimized Cu FCC (111), (110), (211), and (210) surfaces.

Results and discussion

Here we present the results obtained starting from an ideal Cu (211) surface simulated at 700 K. Figure 1a shows how the (211), ideally composed only of green native SOAP sites at 0 K (left), reconstructs local non-native domains, proper of (111), (110) and (210) ideal surfaces (right: yellow, red and blue respectively). Analyzing the population of atomic environments we notice that 40% of native domains disappear and reconstruct non-native domains (Figure 1b). The transition matrix of Figure 1c reports the normalized probabilities for atom transitions between native and non-native environments in the (211) surface (in Δt = 300 ps). The diagonal entries show that only the native (green) and yellow (111) domains have a residence probability >50%, meaning that within these are persistent domains. In contrast, (210) and (110) atomic environments have persistence probabilities well <50%. Such domains are more dynamic, and the atoms composing them have higher probability to re-convert into native domains (red-to-green and blue-to-green transition probabilities 42-43%).

Figure 1. **a** Cu (211) at 0 ns and after 150 ns of MD at 700 K. **b** Equilibrium composition of (211) in terms of native (green) and non-native domains (yellow, blue, red, combined in pink in the inset). **c** Transition matrix showing probabilities for atomic transitions in (211) between native and non-native environments.



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Catalytic Materials Screening by First-Principles and Machine Learning: A case of CO_2 utilization

Supareak PRASERTHDAM[1*], Piyasan PRASERTHDAM[1]

[1]*Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330 Thailand*

[*]*supareak.p@chula.ac.th*

Keywords: Density Functional Theory, Artificial Neural Network, Dry Reforming Reaction of Methane

Introduction. This work demonstrated the improved algorithm based on first-principles and machine learning techniques: density functional theory (DFT) and artificial neural network (ANN). This algorithm is a two-step procedure that comprises catalyst identification and optimization. The Ratings concept was employed to identify the catalyst's reactivity and stability. Each catalyst is given a unique index based on its activation energy obtained from DFT on (1) reactants activation (CH_4 and CO_2) and (2) coke formation and removal benchmarking to the reference catalyst: Ni(111). These indexes on the reactivity and stability surface are used to predict DRM and coking rates at specified operating conditions. Also, the coking boundary proposed in the concept is used to determine the coke-resistant region during DRM. The next step is to generate the database for DRM and coke formation/removal rates of a chosen catalyst at different operating temperatures and CO_2/CH_4 feed ratios. This information is incorporated into the on-line optimization. Ultimately, the goal is to sustain the reaction rate of a given catalyst in the reactor and its coke-resistant property when changes in the condition of the reformer feed composition due to variations of fuel sources are present.

Experimental/methodology. Spin-polarized periodic density functional theory (DFT) calculations were employed via the Vienna ab initio simulation package (VASP). The Projector Augmented Wave pseudopotentials (PAW), plane-wave basis sets, and exchange-correlation functional described within the generalized gradient approximation (GGA) with the functional by Perdew, Burke, and Ernzerhof (PBE) were used for all systems. The Monkhorst-Pack Brillouin zone integration grid of $4\times4\times1$ with the first order Methfessel-Paxton smearing method of 0.2 eV smearing width was used. The convergence criteria are 10^{-4} and 10^{-3} eV for successive electronic and ionic steps. The climbing method nudged elastic band (CI-NEB) was employed to obtain each elementary step's activation energy (Ea). For the Ni oxide, the Hubbard-U correction was used with the GGA-PBE functional with U_{eff} used at 5.4 eV. The assumptions and simplifications of the DRM mechanism were reported in our previous works[4], where the surface reaction is the rate-limiting step. The zero-point energy (ZPE), entropy (S), and internal energy (U) contributions were considered. The pseudo-steady-state hypothesis (PSSH) was applied to determine surface coverages, with no "most abundant reactive surface species" (mari). The $CO_{(g)}$ and $H_{2(g)}$ are assumed to be in the adsorption-desorption equilibrium. Reactivity and stability were illustrated via DRM rate and coke formation from CH and CO and coke removal via H and O, respectively, at a reaction condition of 1000 K with a unity CO_2/CH_4 feed ratio.

Results and discussion. It was demonstrated that the reaction would rapidly proceed on the carbide $Ni_3C(001)$ and the metallic Ni(111) surfaces but would be suppressed on the oxide surface of NiO(100) and the metallic Ni(100) due to the presence of high E_a. Hence, a reactive and stable DRM catalyst would need to be oxide-dominated on the (100) while being metallic-dominated on the (111) facet. On the DRM reactivity, all of the metallic, oxide, and carbide surfaces are active, except NiO(100). Hence, the surface composition that yields reactive and stable Ni-based DRM catalysts is proposed to have less than 10 % of carbide, and up to 75 % metallic is needed.

Acknowledgments

The research has received funding support from the NSRF via the Program Management Unit for Human Resource & Institutional Development, Research and Innovation [grant number B1640034].

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Understanding the interaction of CH_3Cl with Cu-based surfaces

Ingeborg-Helene Svenum[1], Sylvain Gouttebroze[2], Francesca L. Bleken[2]

[1] *SINTEF Industry, P. O. Box 4760 Torgarden, 7465 Trondheim, Norway*
[2] *SINTEF Industry, P. O. Box 124 Blindern, 0314 Oslo, Norway*

Keywords: Rochow-Müller, Copper, CH_3Cl, coke formation

Introduction. In the Rochow-Müller process chloromethyl silanes are made from silicon (s) and CH_3Cl (g), producing $(CH_3)_2SiCl_2$ (M2) as the dominant product. A Cu-based catalyst is needed, which mixes with the silicon forming a Cu-Si alloy. η-Cu_3Si is believed to be the predominant active phase for M2 formation [1]. The system suffers from deactivation and coke formation [2]. The coke formation may be associated with the presence of elemental copper, which is observed post reaction [3]. In this study we investigate the role of copper in the formation of coke precursors, i.e. CH_2, to aid the industrial challenge of hindering these unwanted reactions.

Experimental/methodology. Density functional theory is used to study the decomposition of CH_3Cl and formation of possible coke precursors, CH_2 and CH, on various Cu surfaces, Cu(111), Cu(100), Cu(221) and Cu(410), in addition to Cu-rich Cu-Si models. The DFT calculations were performed using VASP [4], with the PBE functional [5] and an energy cutoff of 550 eV. Adsorption of CH_3Cl and possible decomposition products down to atomic carbon were calculated. Nudged elastic band (NEB) [6] calculations were used to calculate the barriers for CH_3Cl activation and subsequent reaction/decomposition processes.

Results and discussion. The formation of coke precursors (predominantly CH_2) formed in the decomposition of methyl chloride on the surface is compared with a pathway for the formation of the desired product M2. Figure 1 shows the potential energy diagram for the first decomposition step of methyl chloride on Cu surfaces with varying degree of coordination of the atoms in the top-most layer. The first decomposition step to adsorbed CH_3 and Cl is favored compared to C-H bond breaking. The former is a necessary step for the formation of M2 and the separation into paths leading to desired (M2) and undesired (coke precursors) products will be presented.

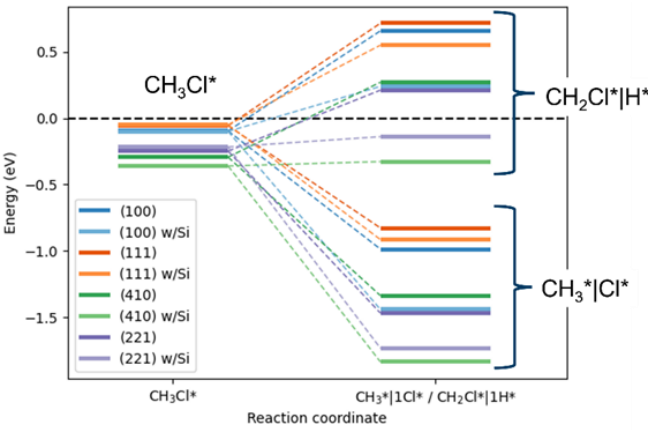

Figure 1. Energy diagram for the first decomposition step for CH3Cl on different Cu(Si) surfaces.

Acknowledgments

This study was performed as part of the HECSI (High Efficiency Silicon for the silicone value chain) project supported by the Norwegian Research Council (project No. 295861) and Elkem ASA. The calculations were performed on resources provided by UNINETT Sigma2 through account no. NN9462K.

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Towards CO_2 hydrogenation: A combined XPS and DFT study on In_2O_3(111) model crystals

Sabrina M. Gericke[1], Minttu M. Kauppinen[2], Margareta Wagner[3], Michele Riva[3], Giada Franceschi[3], Alvaro Posada-Borbón[2], Alexei B. Preobrajenski[4], Lisa Rämisch[1], Sebastian Pfaff[1], Sara Blomberg[5], Lindsay R. Merte[6], Johan Zetterberg[1], Ulrike Diebold[3], Henrik Grönbeck[2] and Edvin Lundgren[7]

[1] *Division of Combustion Physics, Lunds University, Lund, Sweden*
[2] *Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, Göteborg, Sweden*
[3] *Institute of Applied Physics Vienna University of Technology, Vienna, Austria*
[4] *MAX IV Laboratory, Lund University, Lund, Sweden*
[5] *Department of Chemical Engineering, Lund University, Lund, Sweden*
[6] *Department of Materials Science and Applied Mathematics, Malmö University, Malmö, Sweden*
[7] *Division of Synchrotron Radiation Research, Lund University, Lund, Sweden*
[*] *sabrina_maria.gericke@forbrf.lth.se*

Introduction. In_2O_3-based catalysts have shown high activity and selectivity for CO_2 hydrogenation to methanol. The origin of this high performance is, however, still under debate.

Experimental/methodology. To improve the understanding of the surface chemistry of In_2O_3, we studied the reactivity of an In_2O_3(111) single-crystalline film [1] and investigated the adsorption of CO_2 on In_2O_3(111) in a combined X-ray photoelectron spectroscopy (XPS) and density-functional theory (DFT) study.

Results and discussion. Different surface terminations of In_2O_3(111) have been reported in the literature [2,3]. We have investigated the effect of these different surface terminations on the adsorption of CO_2 on the In_2O_3(111). The experiments show that the CO_2 adsorption is hindered on hydroxylated In_2O_3(111) compared to the stoichiometric and the reduced surface. This shows that the hydroxyl groups block the CO_2 adsorption. The CO_2 appears to adsorb as a carbonate on all surface terminations.

Additionally, we studied the effect of the pressure gap on this system (Figure 1). NAP-XPS measurements showed the formation of a new chemical species at 1 mbar CO_2 that might originate from HCOO. Furthermore, the addition CO to the CO_2 and H_2 gas mixture appears to cause the formation of O-CH_3 groups, indicating that CO in the syngas mixture might be crucial for CO_2 hydrogenation over In_2O_3 catalysts.

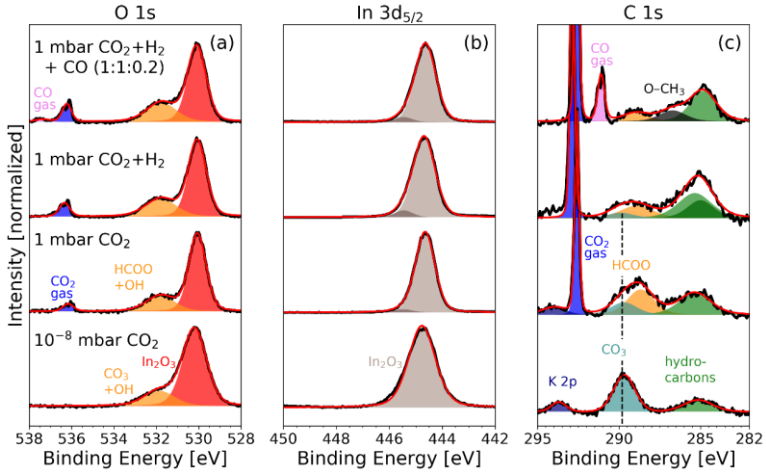

Figure 1: XPS and NAP-XPS measurements of In_2O_3(111) in different gas compositions.

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A DFT Study on the Role of Oxygen Vacancy on m-ZrO_2 ($\bar{1}11$) in Adsorption and Dissociation of CO_2

D. M. Ozkan[1,2], A. Uzun[1,2,3], B. S. Caglayan[2,3], A. E. Aksoylu[1,2*]

[1]*Department of Chemical Engineering, Boğaziçi University, Bebek, Istanbul 34342, Turkey*
[2]*SNG&HydTec Lab, Science and Technology Building, Boğaziçi University, Kandilli, Istanbul 34684, Turkey*
[3]*Advanced Technologies R&D Center, Boğaziçi University, Bebek, Istanbul 34342, Turkey*
[*]*aksoylu@boun.edu.tr*

Keywords: m-ZrO_2, DFT, CO_2 Adsorption, Oxygen vacancy, CO_2 Dissociation

Introduction. The performance stability of a Catalytic Dry Reforming of Methane (CDRM) catalyst is primarily determined by its ability to resist coke formation. This is possible through removal of carbon deposited on the hydrogen production sites of the catalyst by mobile surface oxygen formed via CO_2 dissociation. In this study, it is aimed to understand the role of oxygen vacancies in activation and dissociation of CO_2 molecule on m-ZrO_2, which has been widely studied as the support of CDRM catalysts.

Computational. All periodic DFT calculations in this study were carried out using (CASTEP). Exchange and correlation were included through the use of GGA-PBE functional. The plane-wave cut-off energy was determined to be 640 eV and 6 × 6 × 6 k-point mesh was chosen for the Brillouin Zone (BZ) sampling. m-ZrO_2($\bar{1}11$) surfaces were modeled as a four-layer slab with a vacuum layer of 12 Å along the z-direction. Oxygen vacancy formation on m-ZrO_2($\bar{1}11$) surface was investigated. Then, CO_2 adsorption onto both stoichiometric and nonstoichiometric m-ZrO_2($\bar{1}11$) surfaces were performed. The surface, adsorption and vacancy formation energies were calculated. Local density of states (LDOS) analysis was performed.

Results and discussion. The DFT calculations of oxygen vacancy formation showed that on the m-ZrO_2($\bar{1}11$) surface, the formation of 2-fold coordinated oxygen vacancy is favorable, indicated by its lower formation energy compared to others. Moreover, among 3-fold coordinated sites, removing the ones which are bonded to coordinatively unsaturated Zr atoms is easier compared to ones which are bonded to 7-fold coordinated Zr atom. The results of CO_2 adsorption on the stoichiometric m-ZrO_2($\bar{1}11$) surface revealed that even if strong adsorbate-metal oxide support interaction is present, dissociative adsorption of CO_2 is not observed. Instead, CO_3^{2-} species were formed. On the other hand, spontaneous dissociation of CO_2 molecule was observed on the nonstoichiometric m-ZrO_2($\bar{1}11$) surface. In the final configuration, it was seen that the dissociated oxygen fills the vacancy and CO moiety approaches to either one of the NN cus Zr atom (Figure 1). The results showed that adsorption energies are significantly lower for the nonstoichiometric m-ZrO_2($\bar{1}11$) surface and CO_2 prefers the vacancy sites over other surface oxygen atoms. This implies that CO_2 adsorption on a surface with an oxygen vacancy is energetically more favorable than that on a clean, undefected surface.

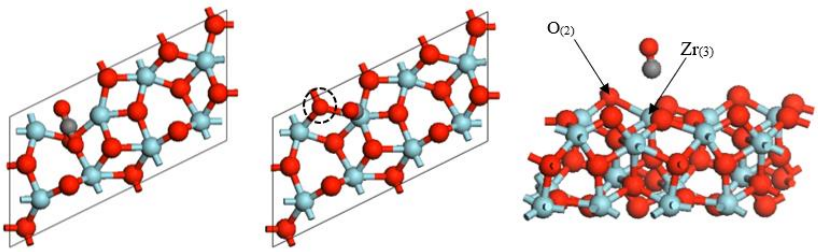

Figure 1. On the left-hand side initial configuration and on the right-hand side top view and side view of the final configuration of the CO_2 molecule on the nonstoichiometric m-ZrO_2 ($\bar{1}11$) surface with a 3-fold vacancy at $O_{(2)}$ location: Initially CO_2 on $O_{(L2)}$.

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CO_2 activation on Ni(111) model catalysts at ambient conditions

R. Ben David[1*], A. Ben Yaacov[1], B. Eren[1]

[1]*Weizmann Institute of Science, Rehovot, Israel*
[*]*Roey.ben-david@weizmann.ac.il*

Keywords: CO_2 activation, Dissociative adsorption, Ni(111) model catalyst, Infrared specroscopy.

Introduction.

The adsorption and activation of CO_2 on metal surfaces is an elementary step to consider for the rational design of catalytic systems for CO_2 conversion and utilization via heterogeneous catalysis [1-2]. Ni-based catalysts are considered to be efficient materials for several CO_2 conversion reactions such as dry methane reforming (DMR), CO_2 methanation, and CO_2 conversion to CO via the reverse water gas shift (RWGS) reaction. The interaction between CO_2 and Ni surfaces at ambient conditions have been recently studied with ambient pressure x-ray photoelectron spectroscopy (AP-XPS) [3-4]. Yet, the exact nature of the surface species and the chemical state of the surface are highly controversial.

Experimental/methodology.

We studied the interaction of CO_2 with metallic and oxidized Ni(111) model catalysts under 1 mbar CO_2 pressure in the temperature range of 25-300 °C using polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS) and Auger electron spectroscopy (AES). Our *in-situ* PM-IRRAS measurements provided information on the molecular surface species and their adsorption sites, whereas AES was used for *ex-situ* analysis of surface oxygen.

Results and discussion.

Our results suggest that CO_2 is dissociatively adsorbed on Ni(111) under ambient conditions. This dissociative adsorption produces CO and atomic oxygen; two strongly bound species which compete for the same preferred adsorption sites, namely the hollow sites. At 25 °C, the produced CO adsorbs mainly on hollow sites, and small fraction adsorbs on top sites. After heating to higher temperatures, the CO occupancy on top sites increases, as more atomic oxygen is produced and blocks the hollow sites. Overall, the surface temperature determines the site occupancy distribution of the CO product during CO_2 dissociation on Ni(111). On oxidized Ni(111) surface, CO_2 dissociation is rather inactive at 25 °C, however, heating the surface to higher temperatures (≥ 200 °C) reduces the oxide layer and exposes metallic Ni. Thus, both bare and oxide-covered Ni(111) surfaces have the same equilibrium chemical state and adsorbed species after heating to elevated temperatures. We attribute the reduction of the oxide layer to residual hydrogen impurities, which efficiently convert atomic oxygen into water vapor.

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Enhanced stability of sub-nanometric Iridium decorated graphitic carbon nitride for H_2 production upon hydrous hydrazine decomposition

Silvio Bellomi*[1], Ilaria Barlocco[1], Xiaowei Chen[2], Juan J. Delgado[2], Rosa Arrigo[3], Nikolaos Dimitratos[4], Alberto Roldan[5], Alberto Villa[1]

[1] *Dipartimento di Chimica, Università degli Studi di Milano, Italy.*
[2] *Departamento de Ciencia de los Materiales, Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz, Spain*
[3] *School of Science, Engineering and Environment, University of Salford, Manchester, United Kingdom.*
[4] *Dipartimento di Chimica Industriale "Toso Montanari", Alma Mater Studiorum Università di Bologna, Italy*
[5] *Cardiff Catalysis Institute, Cardiff University, United Kingdom.*

* *silvio.bellomi@unimi.it*

Keywords: Ir-clusters, Ir-support effect, sub-nanometric, hydrogen economy, heterogeneous catalysts.

Introduction: Stabilizing metal nanoparticles is vital for large scale implementations of supported metal catalysts, particularly for a sustainable transition to clean energy. Indeed, despite the intriguing properties of sub-nanometric metal clusters, one of the biggest challenges is still finding practical ways to stabilise them against migration and ripening phenomena.[1] Recent works indicated graphitic carbon nitride (GCN) as an ideal support for this purpose, due to its peculiar electronic structure and the N-rich framework composed of amine-bridged tri/heptazine moieties.[2] Herein, we report the synthesis of 1 wt% iridium sub-nanometric particles deposited on commercial graphite (Ir/graphite) and on graphitic carbon nitride (Ir/GCN) by a wet impregnation method. We have investigated the metal-support interaction during the hydrous hydrazine ($N_2H_4 \cdot H_2O$) decomposition reaction. $N_2H_4 \cdot H_2O$ is one of most promising hydrogen carriers, a carbon-free fuel with a hydrogen content of 8.0 wt%. It reported to decompose in two different routes: the complete reforming pathway, where H_2 and N_2 are produced, and the incomplete decomposition pathway, i.e., the thermodynamically favored process, producing N_2 and NH_3.[3]

Experimental/methodology. Liquid $N_2H_4{\cdot}H_2O$ decomposition was performed at a constant reaction temperature of 323 K, in a batch reactor connected to a pressure detection sensor, the *Man On the Moon X102 kit*. Fresh and used catalysts were characterized by HR-TEM and XPS in combination with computational techniques. These allowed deep understanding on the role of metal-support interactions on the particle activity and stability.

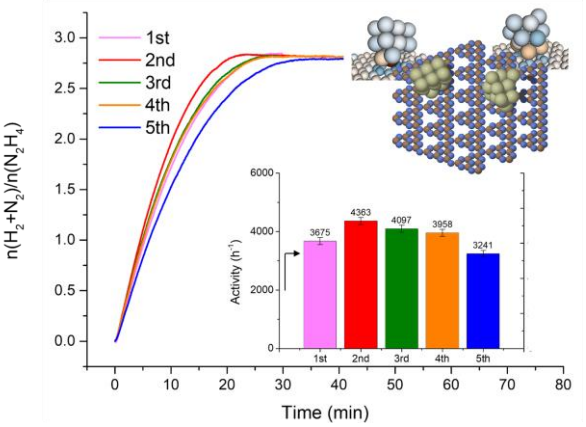

Figure 1 Hydrazine decomposition stability tests for 1%Ir/GCN. Inset is the charge transfer representation for Ir clusters deposited on the typical GCN sites.

Results and discussion. Both catalysts exhibited remarkable initial catalytic activities (3654 h^{-1} and 4024 h^{-1}, respectively) in the hydrous hydrazine decomposition. Recycling tests evidenced an enhanced stability of the Ir/GCN samples upon repeated reaction cycles (Figure 1), without significant modification of the catalyst's structure compared to Ir/graphite, prone to leaching and agglomeration of the sub-nanometric clusters. The enhanced stability was rationalized at an atomic scale level through a combined TEM, XPS and DFT analysis. The combined experimental-computational approach allowed to precisely assign the GCN nitrogen anchoring sites as the main responsible for the sub-nanometric particles integrity and improved stability, and to rationalize the experimental reactivity and characterization results in terms of metal-support interaction. Overall, the enhanced charge transfer due to the N moieties allowed to better stabilise Ir nanoparticles, and in particular the sub-nanometric ones, ensuring high activity under operative conditions.

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Epitaxial growth of ultrathin CoOx films and their interaction with water

M. Cieminski[1], M. C. Schmidt[1], J. Smyczek[1], P. Hubert[1], S. Schauermann[1*]

[1]*Institut für Physikalische Chemie der Christian-Albrechts-Universität zu Kiel, Kiel, Germany*
[*] *schauermann@pctc.uni-kiel.de*

Keywords: Model Catalysis, Cobalt oxide, Thin Films, STM, LEED, Water interaction

Introduction.

Coxide-based based materials recently gained significant importance as efficient heterogeneous catalysts in a variety of reactive processes. In this study, ultrathin CoO_x films were epitaxially grown on Pd(100) and Au(111) single crystals as proxies to powdered catalytic materials. The major focus of this study was on the dependence of the structural properties on the preparation parameters and film thickness.

Experimental/methodology.

The structural composition, termination and the stoichiometry of these films were investigated at the atomistic level by a combination of scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) combined with the calibration via quartz microbalance.

Results and discussion.

Specifically at the lowest Co deposition, the two most prominent co-existing structural domains were identified as c(4x2)/CoO(100)/Pd(100) and bridging oxygen (BO)-CoO_x/Pd(100). With growing nominal Co coverage, the domain with the structural composition c(12x2)/CoO(111)/Pd(100) develops, while the amount of c(4x2)/CoO(100)/Pd(100)- and the BO-CoO_x/Pd(100) domains reduces. Further observed structures include Moiré-CoO(111)/Pd(100) and Co_3O_4(111)/Pd(100), which appear rather at higher Co coverages. Water interaction with two co-existing surfaces c(4x2)/CoO(100)/Pd(100) and BO-CoO_x/Pd(100) was investigated in a broad H_2O coverage range. Specifically, we could show that water readily adsorbs and dissociates on BO-CoO_x/Pd(100) terminated surface, while c(4x2)/CoO(100)/Pd(100) is nearly inert with respect to H_2O dissociation. Further characterization of the H2O-derived adsorbates on the BO-CoO_x/Pd(100)-structure enabled distinguishing three species: two of them could be assigned to OH groups on different adsorption sites – cobalt atoms and bridging oxygen rows. The third identified species can be most likely related to complexes containing non-dissociated water molecules.

The time-resolved catalytic activity of 2D material-supported catalysts at the single active site level

I. Danylo[1*], L. Koláčný[1], V. Svobodová Pavlíčková[2], S. Rimpelová[2], T. Hartman[3], M. Pitínová[1], M. Veselý[1*]

[1] *Department of Organic Technology, University of Chemistry and Technology, Prague, Czech Republic*
[2] *Department of Biochemistry and Microbiology, University of Chemistry and Technology, Prague, Czech Republic*
[3] *Department of Inorganic Chemistry, University of Chemistry and Technology, Prague, Czech Republic*
[*] *danyloi@vscht.cz* (I.D.); veselyr@*vscht.cz* (M.V.)

Keywords: 2D materials; Platinum nanoparticles deposition; Single-molecule fluorescence microscopy; Reaction rate constant of the specific active site; Catalytic activity at the single-nanoparticle level

Introduction. Graphene and other 2D materials are receiving intense attention, driven by their unique chemical and physical properties. During the past decade, graphene, as a typical member of the 2D material family, has been widely investigated for catalysis. However, graphene could also be used as a 2D support for metal NPs [1]. These catalytic systems exhibit a significant increase in a catalytic activity and selectivity. The explanation of the increased activity and selectivity is usually reduced to the electronic properties of the 2D support and the specific interaction between NPs and the support [1]. To investigate these interactions and the support effect on a catalytic activity, it is necessary to obtain the same uniform pattern of metal NPs on different types of 2D supports. Electron Beam Lithography (EBL) enables to help with the precisely controlled nanofabrication of metal NPs. The advantage of this method is direct and target depositions on the selected 2D sheet features with the known size and spatial distribution. Due to a super-resolution, single-molecule fluorescence microscopy (SMFM) is used to determine a time-resolved catalytic activity at the single active site level using the localization of single molecules (reaction turnovers). SMFM has been demonstrated to be a powerful technique for the visualization of reaction behaviors and can be employed to record single reaction turnovers using fluorogenic molecules. Each turnover is represented by a single reaction track, from which catalytically active zones in the material can be reconstructed with a super-resolution. Because reaction events occur stochastically at the active catalyst sites, these tracks are spatially and temporally separated and can be resolved individually for each turnover [2]. These studies primarily focus on quantitative imaging of a time-resolved catalytic activity at a single active site level due to SMFM, which is eble to reveal the behavior of individual reaction turnovers.

Experimental/methodology. The platinum NPs deposited onto two types of 2D support materials by EBL were tested for a catalytic activity at a single active site level using a super-resolution fluorescence microscope. As a result, we acquired time-resolved image series that contained single-molecule reaction turnovers. Then, the microscopic activity map was produced by integrating images over the reaction time.

Results and discussion. In this study, we evaluated the time- and spatially-resolved microcatalytic activity of the same metal NPs on various supports and calculated an overall reaction rate constant for the specific active sites. We also determined the lifetimes of fluorescent (active) and non-fluorescent (dark) states for each active site. The comparison of kinetic characterization for two different supported catalysts demonstrated that the second catalyst had the longer lifetime of a dark state (τ_{off} = 5.72 × 10^{-2} s compared to τ_{off} = 4.05 × 10^{-2} s). This led to a decrease in the reaction rate constant (17.48 ± 0.22 s^{-1} compared to 24.69 ± 0.22 s^{-1}) and, as a result, reduced the working quality of the catalyst. Therefore, this approach enabled us to understand how the catalytic activity of a specific active site can affect on the catalytic properties of 2D material-supported catalysts.

Acknowledgments
This project was supported by the Czech Science Foundation (GACR No. 23-08083M) and the grant of Specific university research – grant No A2_FCHT_2023_088.

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Ni-Mo nanoparticle generation by spark discharge

Jonas Elmroth Nordlander[1] *, Marie Bermeo[2] , Pau Ternero[2] , David Wahlqvist[3], Toni Schmeida[4], Sabrina Gericke[2], Filip Hallböök[1],
Maria E. Messing[2] , Martin Ek[3], Julia-Maria Hübner[3] Sara Blomberg[1],
[1] *Department of Chemical Engineering and NanoLund, Lund University, Box 124, 22100 Lund, Sweden*
[2] *Department of Physics and NanoLund, Lund University, Box 118, 22100 Lund, Sweden*
[3] *Department of Chemistry and NanoLund, Lund University, Box 124, 22100 Lund, Sweden*
[4] *Leibniz-Institut für Festkörper- und Werkstoffforschung, Helmholtzstraße 20, 01069 Dresden, Germany*
* *Correspondence: jonas.elmroth_nordlander@chemeng.lth.se*

Keywords: metal nitrides; HDO; nanoparticles; spark discharge; carrier gas

Introduction. Ni-Mo catalysts are important in many different catalytic applications [1-3], such as hydrodesulfurization (HDS) [1,3] and hydrodeoxygenation (HDO) reactions [1]. To develop these catalysts further detailed knowledge about the properties of the material is needed. However, the active supported catalysts are complex and fundamental studies are challenging, due to the low concentration of the active phase. As such, model systems with a high concentration of the active phase are useful for elucidating the properties of catalytic systems.

In this study, we design a model system of well-defined nanoparticles generated by a spark discharge method. The spark discharge method offers the possibility of creating and depositing catalytically active nanoparticles of well-defined size, allowing for the construction of high-concentration model systems where the active phase can be studied in isolation. While this method has already been used to synthesize oxides [4] and hydrides [5], we can in this study also report, for the first time, of the synthesis of nitrides using this technique. Here, we present the successful spark-discharge synthesis and characterization of different phases of Ni-Mo nanoparticles.

Experimental/methodology.

Nanoparticles were generated using a previously-described spark discharge set-up and method [6]. Briefly, $Ni_{30}Mo_{70}$ electrodes with a separation of 1.5 mm were used as a material source, while 5 % H_2 in N_2 was used to prevent oxidation. Compaction was carried out at 1200 °C, and certain samples were size-filtered using a DMA. Oxidation of as-deposited nanoparticles was carried out in air at 400 and 510 °C.
Structural and compositional analysis was carried out using TEM, SAED, STEM-EDX, EELS and PXRD.
Further, synchrotron-based XPS studies following the H_2 reduction of the oxides were performed where the chemical compositions could be followed in situ.

Results and discussion. TEM and STEM-EDX imaging on as-deposited particles indicated the formation of Janus particles consisting of a pure Mo and a Ni/Mo phase, as illustrated in Figure 1. The presence of the oxides as well as nitride was further confirmed by TEM and STEM/EDX. The successful synthesis of NiMo nanoparticles opens up the possibility of in-detail mechanistic investigations of industrially important catalyst systems.

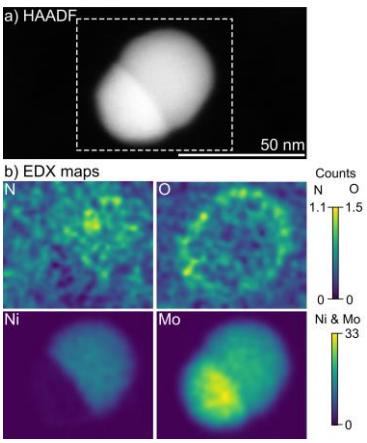

Figure 1: HAADF-STEM and STEM-EDX images of as-deposited Ni-Mo nanoparticles.

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Anharmonic Correction to the Adsorption Free Energy by Machine Learned Force Field-based Thermodynamic Integration

Thanh-Nam Huynh[1], Dmitry Sharapa[1], Tomáš Bučko[2,3], and Felix Studt[1,4]*

[1]*Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany*

[2]*Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, SK-84215 Bratislava, Slovakia*

[3]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-84236 Bratislava, Slovakia*

[4]*Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany*

**felix.studt@kit.edu*

Introduction. An accurate description of adsorption process is of paramount importance for the understanding of heterogeneous catalytic process. However, the current approaches of adsorption free energies calculations either provide insufficient entropic contributions or are very complex and/or computationally expensive. The harmonic approximation (HA), the method that has been utilized most frequently thus far, is prone to significant deviations [1]. There is need in method that is able to recover the free energy contributed from a system's anharmonicity for a better description of free energy.

Herewith, we present a new approach, in which machine learned force field (MLFF) is used in place of DFT in the most time-consuming step of λ-path thermodynamic integration (MLFF-based λ-TI) in order to calculate the anharmonic contribution to free energies. This allows us to reach accurate free energies of adsorption processes, which could then provide more insight into the reaction mechanism of surface reactions.

Results and discussion. First, a model system of ethane (C_2H_6) was used to assess the applicability of the MLFF-based λ-TI method. Table 1 shows an excellent agreement in the free energy due to anharmonicity of the system resulted from MLFF-based λ-TI and from DFT-based λ-TI [2], in comparison with semi-analytical solution. An accuracy of mili-electronvolts makes it reasonable to apply the method for more realistic and complicated system of interest.

Table 1 The anharmonic corrections ΔA0,q→1 (in meV) determined by MLFF-based TI compared with DFT-based TI and semi-analytical solutions (if available).

$\Delta A_{0,q\to1}$	MLFF	DFT	Semi-analytic
C_2H_6	-3.27	-3.30	-4.1
OH@Pt(111)	-250.0	-	-

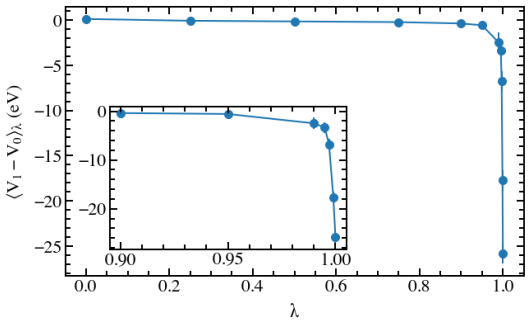

Figure 1 Averaged energy differences obtained by MLFF-based MD runs at 400K

Figure 1 provides the energy differences for TI of the OH@Pt(111) system obtained by MLFF-based MD simulations. As the behaviors of the system change rapidly when it comes closer to the fully interacting regime, more points were added (λ = 0.90, 0.95, 0.99, 0.995, 0.997, and 0.999) to smooth the curve, resulting in 11 λ points in total. The computed anharmonic correction for this system gives a significant value of -0.250 eV, which is as high as roughly 12.5% of the harmonically approximated adsorption free energy (-2.01 eV).

This method allows for fast and accurate calculations of adsorption and desorption free energies, which could pave the way for detailed and precise predictions of equilibrium and rate constants for surface reactions.

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Role of Na^+ on the Stability of Zeolite-supported Molybdenum Sulphide Clusters using *ab initio* Calculations

J. Iyer[1,2], T. S. Khan[3], D. J. Searles[2], M. A. Haider[1*], R. Khare[4], J. Lercher[4]

[1]*Indian Institute of Technology Delhi, New Delhi, India;* [2]*University of Queensland, Brisbane, Australia;*
[3]*Indian Institute of Petroleum, Dehradun, India;* [4]*Technical University of Munich, Munich, Germany*
[*]*haider@iitd.ac.in*

Introduction. Transition metal sulfides (TMS) are important commercial catalysts for hydrotreating processes like hydrodesulfurization, hydrodeoxygenation, hydrodearomatization. In this class of catalysts, molybdenum sulfide is the focus of more research than other catalysts due to its resistance to deactivation in comparison to other transition metals such as Pd, Pt, etc. In a move towards understanding catalyst performance, Lercher and co-workers presented the efficacy of Mo_2S_4 clusters finding that it differed from that of the traditional MoS_2 slabs [1, 2]. These catalysts were compared based on their reactivity and stability during ethylene hydrogenation to ethane. Due to the absence of Brønsted acid sites, the NaY zeolite support for Mo_xS_y clusters was not active for ethylene hydrogenation. The comparison of ethane formation rate showed a stable reactivity for over 150 hours on molecular Mo_2S_4 clusters, much longer than on a MoS_2 slab. Therefore, there is a need for deep mechanistic understanding of Mo_2S_4 cluster stability and reactivity in NaY zeolites using ab initio calculations.

Methodology. Two NaY zeolite models are tested with different Na^+ ion positions as shown in Figure 1 while maintaining the experimental Si/Al ratio of ~2.5. For stable positions of Mo_2S_4 cluster in these zeolites, we compared two pathways for ethene hydrogenation over the cluster to decipher the role Na^+ ions on the reactivity using density functional theory. In addition, to obtain further insights into the role of Na^+, we carried out Bader charge analysis and analysed the dynamics of Mo_2S_4 clusters using ab initio molecular dynamics (AIMD). The ab initio calculations were carried out on Vienna ab intio simulation package (VASP).

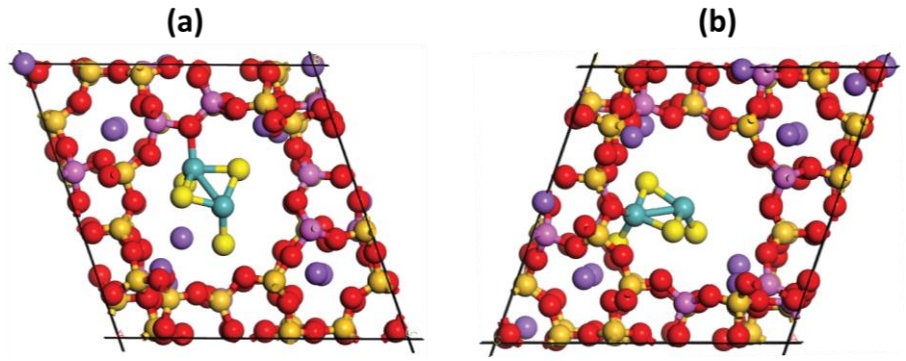

Figure 1. Anchored Mo_2S_4 cluster in NaY zeolite supercage. The two models showcase different Na^+ positions– (a) Na^+ present, and (b) Na^+ absent in the supercage Here, spheres in cyan, yellow, red, orange, pink and majenta represent molybdenum, sulphur, oxygen, sulphur, aluminium, and sodium, respectively.

Results and discussion. On analysing the activation barriers for ethene hydrogenation, we observed that with and without Na^+ in close vicinity to the Mo_2S_4 cluster, the 1st hydrogenation barrier changed by ~40 kJ/mol without altering the pathway. The Bader charge analysis showed that the charge transfer between Na^+ and Mo_2S_4 in the zeolite is not influenced by Na^+ position, thus suggesting that charge transfer does not affect the reactivity. The charge analysis showed a neutral Mo_2S_4 cluster and an average +1 charge on Mo atoms at different binding configurations. Therefore, we explored the dynamics of anchored Mo_2S_4 with different Na^+ positions. The AIMD simulations helped us to quantify that Na^+ plays an important role in cluster stability by providing a steric hinderance to their movement resulting in the change in hydrogenation barrier.

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Theoretical studies investigating the mechanism of methanol formation over a Cu/ZnO based catalyst

David A. Jurado A.[1], Michael D. Higham[2], C. Richard A. Catlow[2], Ingo Krossing[1]
[1]*Universität Freiburg, Institut für Anorg. & Analyt. Chemie 79104 Freiburg, Germany*
[2]*University College London, Dept of Chemistry, WC1H 0AJ London, UK*
[*]*david.jurado@ac.uni-freiburg.de*

Introduction.

Cu/ZnO-based catalysts have been used to synthesize MeOH from syngas ($CO/CO_2/H_2$) for almost 60 years. Methanol production is a major industrial process, reaching 311 million tons per year in 2030 and growing. However, the mechanism of MeOH formation via CO_2 hydrogenation remains under discussion. Key areas of debate are the role of O defects/ vacancies on the ZnO surface, Cu-Zn synergism at the interface, the formation of Cu/Zn alloys, the role of ZnO (i.e. SMSI), etc.[1,2,3]

Experimental/methodology.

All periodic DFT calculations were performed using the software *VASP*. The electronic structure was calculated using PAW approximation for the core-valence interactions and PBE_{Sol} as exchange-correlation functional. The plane wave cut-off was set at 450 eV and the gamma point was used as k-point. The system consists of 230 atoms in a 3D periodic slab model[4]. Bulk lattice parameters are a = 3.2518 Å, c =5.1969 Å, u = 0.3806. The system consists of 6 ZnO layers plus an 8 Cu atoms cluster. All Cu atoms and the top 3 ZnO layers are allowed to relax during structural optimisation until atomic forces converged to within 0.05 eV $Å^{-1}$. Other layers were fixed. The slabs are interleaved by an 18 Å vacuum.

Results and discussion.

Using computational resources, all relevant intermediates to the MeOH synthesis were investigated on a realistic model catalyst surface (a Cu cluster on a reconstructed polar ZnO surface).[4] We provide a detailed analysis of the different surface sites, stabilities, activation of the intermediates on the surface and activation barriers for relevant elementary processes. Our analysis explains that MeOH would be form following the path CO_2*→HCOO*→H_2COO*→H_2COOH*→H_2CO*→H_3CO*→MeOH on the interfacial Cu/Zn site of a Cu/ZnO catalyst.

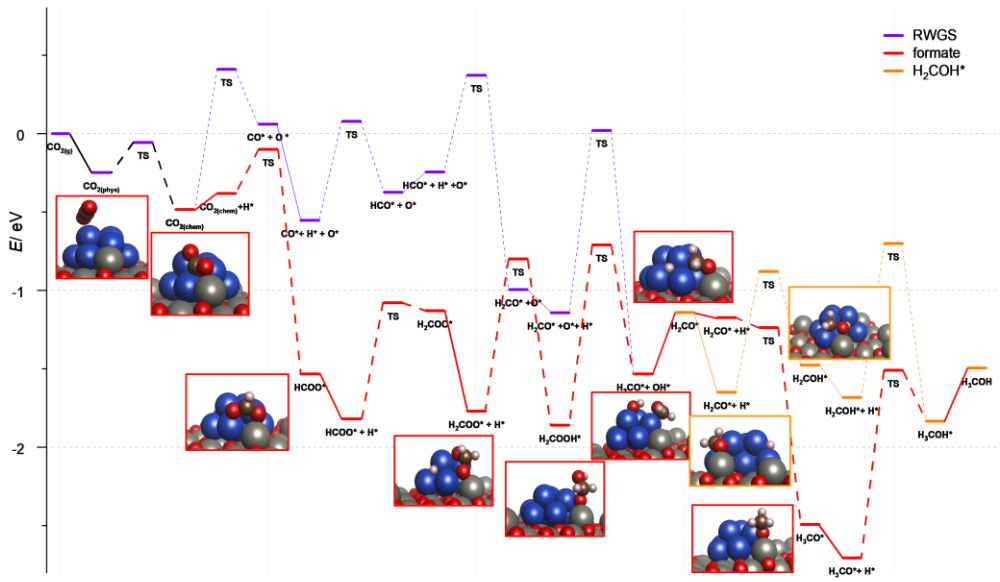

Figure 1: Energetic pathway of intermediates of the CO_2 hydrogenation via formate pathway and RWGS to form methanol on a model Cu/ZnO system. For the images red is reserved to O atoms, brown for C, blue for Cu, grey for Zn and white for H. Transition states (TS) are denoted with dashed lines.

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The effect of Ethylene-Vinylacetate(EVA) on the properties of the UHMWPE fiber-reinforced composite

E.H Kang[1], J.H Kim[2], N.Y Jang[3], S.G Lee[1*]

[1]*Department of Applied Organic Materials Engineering, Chungnam National University, Daejeon, Korea*
[2]*Research Institute for Applied Chemistry and Biological Engineering, Daejeon, Korea*
[3]*Department of Organic Materials Engineering, Chungnam National University, Daejeon, Korea*
[*]*lsgoo@cnu.ac.kr*

Keywords: UHMWPE, fiber-reinforced composite, ethylene-vinylacetate, impact strength

Introduction.

Ultra-high molecular weight polyethylene(UHMWPE) fibers have excellent chemical resistance and impact resistance, and have low density, so they have excellent specific strength and specific modulus compared to other reinforced fibers. Due to these characteristics, it is widely used as a reinforcement material for high-performance polymer matrix composites, especially in the fields of hiking supplies, aerospace materials, and bulletproof materials.[1]

In order to prepare a fiber-reinforced composite using UHMWPE fiber, polyolefin elastomers(POE) with excellent ductility and low shore hardness were selected among thermoplastics elastomers. By borrowing the hot melt impregnation process, a prepreg was manufactured using a hot press machine, but impregnation was not properly performed at a temperature at which the fibers were not damaged.

In this study, ethylene-vinyl acetate(EVA) used as an adhesive was mixed with POE to increase the adhesion characteristics with fibers at low temperatures. The effect of EVA on the physical properties of UHMWPE fiber-reinforced composite was examined by analyzing the impact strength, peel strength, and morphology of composite materials applied with different composition ratios of POE and EVA.

Experimental/methodology.

Compound the content of EVA resin relative to POE at 0, 10, 20, 30, and 40 wt% at 120-180℃. The film according to EVA content is impregnated into the UHMWPE fabric by applying heat and pressure through a hot press machine to obtain prepreg. These prepregs are laminated at [0/90°] and then pressed to produce the final UHMWPE fiber-reinforced composite.

Results and discussion.

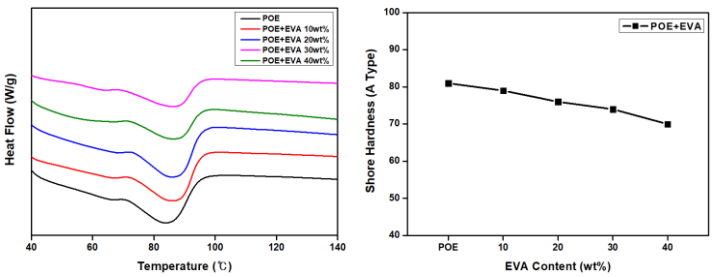

Figure 1. DSC curves and shore hardness of POE films according to EVA content.

When EVA is added to the amorphous POE resin, some crystallinity is given, and T_m tends to increase slightly. However, the shore hardness of the film tends to decrease as the EVA content increases.

Acknowledgments

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Computational and surface science studies on the properties of In_2O_3 for methanol synthesis

M. M. Kauppinen[1*], S. M. Gericke[2], M. Wagner[3], M. Riva[3], G. Franceschi[3], A. Posada-Borbòn[1], L. Rämisch[2], A. B. Preobrajenski[2], S. Pfaff[2], A. M. Imre[3], S. Blomberg[2], L. R. Merte[4], J. Zetterberg[2], U. Diebold[3], E. Lundgren[2], H. Grönbeck[1]

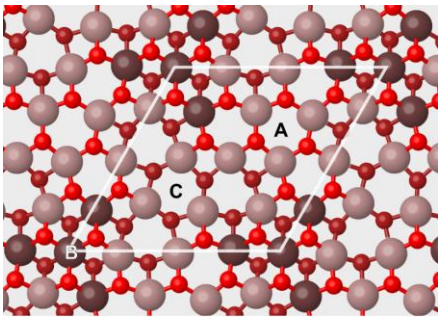
[1] *Chalmers University of Technology, Gothenburg, Sweden*
[2] *Lund University, Lund, Sweden*
[3] *Vienna University of Technology, Vienna, Austria*
[4] *Malmö University, Malmö, Sweden*
[*] *minttum@chalmers.se*

Keywords: Synchrotron-based XPS, Core level shifts, heterogeneous catalysis, density functional theory, oxides, methanol synthesis

Introduction. In_2O_3-based catalysts have shown to be highly selective, active, and stable methanol synthesis catalysts [1]. However, the nature of the active sites is still not fully understood. To advance understanding of the active sites and the effect of water on CO_2 hydrogenation to methanol, fundamental studies of single crystalline In_2O_3 surface in a controlled environment are required. We have employed both experiments and theory to investigate well-defined In_2O_3 surfaces with different surface treatments in order to elucidate the initial steps of the CO_2 hydrogenation reaction.

Experimental/methodology. X-ray Photoemission Spectroscopy (XPS) and Density Functional Theory (DFT) calculations were employed to study CO_2, H_2O, methanol and formic acid adsorption on In_2O_3(111) with different surface terminations, namely, pristine, hydroxylated, and reduced indium oxide[2]. Electronic structure and core-level shift calculations were calculated with the Vienna Ab initio Simulation Package using the Perdew-Buke-Ernzerhof (PBE) and the Heyd-Scuseria-Ernzerhof (HSE06) functionals.

Results and discussion. We were able to identify indium ad-atoms in the In 3d spectra on the reduced surface both with XPS and DFT calculated core-level shifts. On the hydroxylated surface OH-groups give characteristic peaks in the O 1s core level, and we report excellent agreement between the experimental and computed O 1s shifts. These fingerprints of the different surface terminations could be used in future studies at more realistic reaction conditions. In addition, comparison of the experimental C 1s spectra and the DFT calculated core-level shifts suggest that CO_2 adsorbs as a carbonate on all surface terminations. On the hydroxylated surface, we find that CO_2 adsorption is hindered by the presence of hydroxyl groups, which adsorb preferentially at the same site. This in turn could lead to a decrease in methanol synthesis activity, which is in agreement with a previously reported hindering effect of water on the reaction[1].



Stoichiometric In_2O_3(111)

Acknowledgments
This work was funded by the Knut and Alice Wallenberg (KAW) foundation, the Swedish Research Council , the Swedish Foundation for Strategic Research, the Åforsk Foundation, the Crafoord Foundation and the Adlerbertska Foundation. The calculations were performed at PDC via a SNIC grant.

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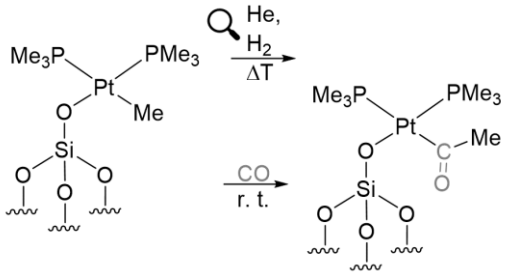
Molecular Model Catalysts of Atomically Dispersed Platinum on Silica

L. Kopietz[1*], K. Köhler[1]

[1]*Technical University of Munich, Munich, Germany*
[*]*lea.kopietz@tum.de*

Keywords: platinum, model catalyst, surface organometallic chemistry

Introduction. For a heterogeneous catalyst, it is still challenging to unravel the active site structure or to gain a deep understanding of the ongoing processes on a molecular level. [1] In academic research, different approaches focus on modeling the (proposed) active site. By that, one expects to get a deeper insight into the relation between structures and their reactivity (or a mechanism), which forms the basis for a more rational catalyst development. [2] Surface Organometallic Chemistry (SOMC) is one approach, which has been particularly successful in unraveling mechanisms due to defined, molecular sites on oxide materials (see Scheme 1). A key aspect thereof is a thorough investigation of the structure and the transfer of established elementary steps from homogeneous catalysis to a yet heterogeneous catalyst. [1]
This work focuses on the structure and reactivity of organometallic platinum complexes, which are immobilized on a pretreated silicon dioxide surface. In particular, changes in the molecular structure, which may be caused by temperature or atmosphere (e. g. CO), allow a deeper insight into the nature of such (potential) single-site catalysts, but also into their limitations (see Scheme 1).
Experimental. Dimethylbis(trimethylphosphine)platinum(II) is obtained in a two-stepped procedure, adapted from literature. [3] It is used afterwards for grafting on silicon dioxide, which has been partially dehydroxylated at 700 °C under high vacuum conditions. This procedure generates isolated, molecular platinum complexes on the silica surface.
Results and discussion. The platinum model catalyst was characterized by means of IR and solid-state NMR spectroscopy (^{1}H, ^{31}P), as well as by elemental analysis. The methods support the successful synthesis and structure of the compound. Structural changes were evaluated as a function of the temperature in different gas atmospheres (helium, hydrogen, carbon monoxide).



Scheme 1: Supported, molecular platinum(II) complex on silicon dioxide, which inserts CO into the Pt-C bond.
For that purpose, CO chemisorption was performed as an *in-situ* IR experiment (1% CO in He, 20 mL min^{-1}, r. t.). Bands of linearly bound carbon monoxide on platinum (2094 cm^{-1}, 2071 cm^{-1}) are observed, as well as the band of an acyl species (1612 cm^{-1}). The latter one suggests the insertion of CO into the platinum-carbon bond and is illustrated in Scheme 1. [4] This reactivity is similar to molecular platinum complexes in solution and supports the molecular character of the platinum surface sites. [4] Ongoing investigations focus on structural changes under reducing conditions.

Acknowledgments
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Computational investigations into the direct synthesis of higher alcohols from syngas on copper–iron catalysts

Ville Korpelin[1*], Bhumi A. Baraiya[1], Hanan H. Ibrahim[1] ,Toni Kiljunen[1], Karoliina Honkala[1]

[1]*Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, 40014, Jyväskylä, Finland*

[*]*ville.p.korpelin@jyu.fi*

Keywords: alcohols, alloys, DFT, heterogeneous catalysis, syngas

Introduction. Higher alcohols (HA) are used as fuel additives, solvents and feedstocks in the production of pharmaceuticals, plasticizers and surfactants.[1] Currently, HA are mostly produced via fermentation (light alcohols) or from petroleum-derived hydrocarbons (heavy alcohols). The direct conversion of syngas to HA is a promising alternative for both environmental and economic reasons, enabling the application of bio-based feedstock in a one-step process. As the pathway involves CO activation, C–C coupling and hydrogenation, an optimal catalyst has to provide multiple functionalities. For this reason, mixtures such as Cu–Fe are among the most promising materials for the process.

Experimental/methodology. The Cu–Fe mixture is modeled as a well-mixed 1:1 alloy, representing the limit of maximum contact between the components. In order to describe typical active sites on a nanoparticle edge, the catalyst was modeled as a stepped CuFe(211) surface (see Figure 1). The DFT calculations were spin-polarized and vdW-corrected, and the transition states were located using the climbing image NEB method.

Results and discussion. The reaction network from CO and H_2 to the typical C1 and C2 hydrocarbons and alcohols (CH_4, CH_3OH, C_2H_6, C_2H_5OH) was simulated, along with selected chain-growth steps toward C3 intermediates. The activation of CO is most favorable at the step edge, as the 4-fold step site can strongly adsorb C and CH. For the C1 intermediates, the CH_n–CH_n coupling, CO insertion and hydrogenation steps are competitive, with hydrogenation being the most favorable both kinetically and thermodynamically. This indicates that methanation is a major process on the alloy, though chain growth and alcohol formation can also occur. The results support the traditional HA synthesis concept of C_nH_m chain growth followed by CO insertion and hydrogenation to primary alcohol; CO insertion is unlikely to be the main chain growth mechanism due to the high C–O cleavage barriers of the intermediates.

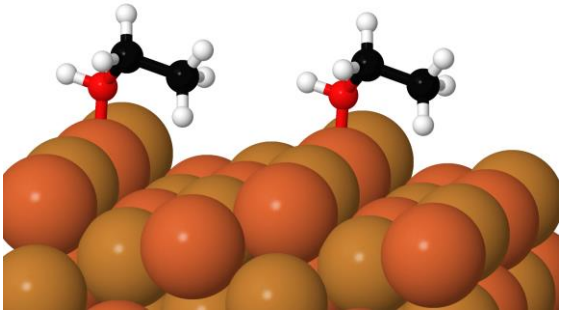

Figure 1: Side view of well-mixed CuFe(211) with adsorbed ethanol.

To clarify the roles of the metal components and the surface geometry, comparisons to alternative surface models are underway. According to the literature and our preliminary machine learning simulations, the surface layer of the binary CuFe mixture is preferably enriched in Cu, although adsorbates such as CO can induce the segregation of Fe to the surface.[2,3] These studies will complement the understanding gained on the perfectly mixed alloy and help identify the key properties of an effective HA synthesis catalyst.

Acknowledgments

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Electric Double Layer effect on outer-sphere benzyl halides electro-reduction mechanism

Aleksandr Kramarenko[1], Dmitry Sharapa[1], Evgeny Pidko[2], Felix Studt[1]

[1]*Karlsruhe Institute of Technology,Karlsruhe, Germany*

[2]*TU Delft, Delft, The Netherlands*

[*]*aleksandr.kramarenko@partner.kit.edu*

Keywords: Electrocatalysis, benzyl halides, DFT, Molecular dynamics

Introduction. Electrochemical CO_2 fixation is a perspective method of carbon dioxide conversion, which does not demand high temperatures and pressure[1]. Moreover, the fixation of CO_2 by electrochemicaly activated benzyl halides is and environmentally friendly and promising way for the synthesis of the important for pharmaceutical and fuel production carboxylic acids derivatives. Therefore, to improve the performance of electrode material and increase product yields, it is important to gain insight into the electrode-electrolyte interplay and the rate-determining reaction steps. The combination of first principles and molecular dynamics simulations gives us a good understanding at the molecular level of charged interface phenomena and allows us to study elementary chemical processes in detail, which sheds light on how to improve electrocatalytic reactivity.

Computational methods. In this study, we used complex approach for benzyl halide electroreduction process simulation. Therefore, we performed non-periodic density functional theory (DFT) calculations[2], in order to assess the standard reduction potentials of benzyl halides, and estimate the mechanism of electrochemical carboxylation reaction, together with the classical molecular dynamics[3] (CMD) to reveal the concentration distribution of the solution components in the EDL region.

Results and discussion. In this study, we have explored the electrochemical activation, and reduction mechanism of benzyl halides and their subsequent electrocarboxylation. Following our multi scale approach we first performed bulk electrolysis simulation in order to investigate the thermodynamic parameters of carboxylation steps in aprotic media. The standard reduction potentials (SRP) calculated for the three benzyl halides in MeCN are reported in Figure 1, and show a repeated shift to the less negative values in the following sequence BnCl < BnBr < BnI.

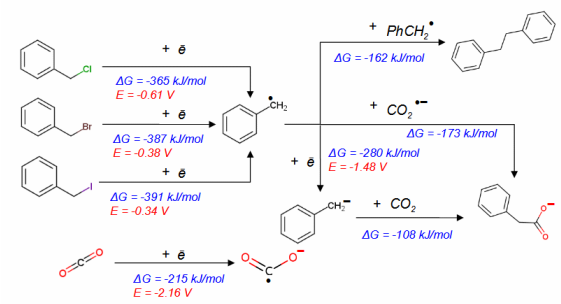

Figure 1. Thermodynamic parameters for the proposed mechanism of electrochemical carboxylation of benzyl halides in acetonitrile solution. (Calculated using CPCM solvation model, the standard reduction potentials are shown with respect to the saturated calomel electrode).

Moreover, experimental results of the electro-reduction process for the studied benzyl halides reveal the same qualitative tendency to our computational results[4]. Subsequent, electron transfer to the produced benzyl radicals has a higher energy barrier, therefore, it has more negative reduction potential. Hence, a simple thermochemical coupling of the benzyl radicals becomes more favorable.

Acknowledgments

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One-step steam reforming of methane to methanol by plasma catalysis: experiments and DFT modelling

Shangkun. Li[1*], Yingzi Hao[2], Yanhui Yi[2*], Kristof M. Bal[1], Nick Gerrits [1], Erik C. Neyts[1], Annemie Bogaerts[1*]

[1]*Research Group PLASMANT, Department of Chemistry, University of Antwerp, Universiteitsplein 1, BE-2610, Wilrijk, Antwerp, Belgium*

[2]*State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian, 116024, PR China*

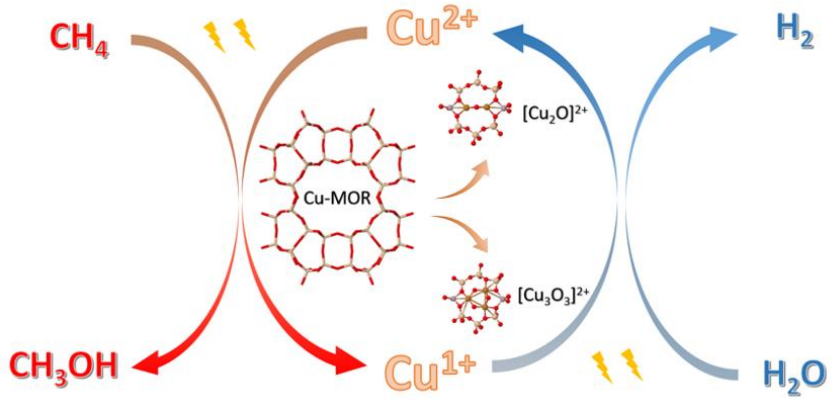
[*]*Corresponding Author's E-mail address: shangkun.li@uantwerpen.be; yiyanhui@dlut.edu.cn; annemie.bogaerts@uantwerpen.be*

Keywords: Plasma catalysis, methane conversion, density functional theory

Introduction. The selective activation and targeted conversion of methane into value-added chemicals is considered a holy grail in catalysis. Plasma technology is a promising approach to activate gas molecules by energetic electrons instead of heat, it can be operated at mild conditions and allows easy upscaling.[1] Our previous study revealed that plasma-catalytic direct oxidation of methane to methanol (DOMTM) could realize 81 % liquid oxygenates selectivity and 50 % CH_3OH selectivity promoted by Ni-based catalysts, at low temperature and atmospheric pressure.[2] Recently, we found that one-step steam reforming of methane to methanol (OSRMTM) via a combination of $CH_4/H_2O/Ar$ plasma with copper-containing zeolite can further increase the CH_3OH selectivity to 82 %, with 4.7 % CH_4 conversion.

Experimental/methodology. The plasma-catalytic OSRMTM setup was the same as in our previous study.[2] All the DFT calculations were carried out in CP2K 7.1 package with Quickstep module and PBE functional. [3]

Results and discussion. Catalyst characterization and plasma diagnostics reveal that the excellent reaction performance is attributed to Cu-O active sites confined by the pore of Cu-MOR zeolite. Furthermore, by dedicated experiments and DFT calculations, we demonstrate the existence of a redox process from Cu^{2+} to Cu^{+} on Cu-MOR, which plays an important role in plasma-catalytic OSRMTM in a continuous flow reactor (Scheme 1). This study provides a fundamental understanding of radical-involved processes taking place and the mutual interactions between plasma and zeolite-confined copper catalyst.



Scheme 1. Schematic of plasma-catalytic OSRMTM via $CH_4/H_2O/Ar$ plasma and Cu-MOR zeolites

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Carbonyl surface modification of Al_2O_3 to synthesize tailored noble metal catalytic sites: from single atoms to sub-nano clusters

Yu-Cheng Lin[1] and Jeremy S. Luterbacher[1*]

[1]*Laboratory of Sustainable and Catalytic Processing, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*
[*] *jeremy.luterbacher@epfl.ch*

Keywords: Carbonyl group surface modification, single atom catalysis, size-controllable noble metal sites and CO oxidaiton

Introduction. Supported noble metals play an important role in heterogeneous catalysis due to their superior catalytic performance. Because of their scarcity, increasing the dispersion and maximizing the use of precious metals species on the catalyst surface have been extensively studied.[1] Recently, single-atom catalysts (SACs), with 100% atom efficiency and higher reactivity compared to their nanoparticle counterpart, have attracted much attention.[2] The conventional way to prepare supported metal catalysts is via the impregnation method. This tends to result in an uneven distribution of particle size with both metal nanoparticles and small clusters on catalyst surface, hindering the formation of single-atom sites.[2] To solve this issue, several methods have been proposed to increase the amount of isolated or highly dispersed metal atoms on the support.[3-4] For example, Christopher et al. synthesized stable Pt single atom sites on TiO_2 by strong electrostatic adsorption of a very low amount of Pt on TiO_2.[5] Lee et al. deposited single noble metal atoms on ceria nanoparticles which were anchored on Al_2O_3.[3] In another study, the doping of La into Al_2O_3 was found to stabilize isolated Pd atoms on the surface.[6] Pd SAC could also be achieved by a photochemical route.[7] However, a more general method to prepare different noble metal SACs as well as small clusters (<2nm) has not yet been proposed.

Experimental/methodology. Here we report a carbonyl surface modification method which helps to increase the dispersion of noble metal species on the Al_2O_3 surface. The surface OH groups of Al_2O_3 support were first changed to carbonyl groups with better ligand strength and affinity toward metal ions, confirmed by Fourier-transform infrared spectroscopy (FT-IR). The surface-modified Al_2O_3 was then used for preparing noble metal SACs (Pd and Pt) and characterized by aberration-corrected scanning transmission electron microscopy (AC-TEM), carbon monoxide diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) and extended X-ray absorption fine structure (EXAFS). The CO oxidation reaction was used to test catalytic activity and the results were monitered by gas chromatography (GC).

Results and discussion. By AC-TEM, CO-DRIFTS and EXAFS, we confirmed that both Pd and Pt SACs can be achieved by this method. Moreover, Pd and Pt clusters with a diameter smaller than 1 nm can also be obtained by adjusting the experimental conditions. In a following CO oxidation test, Pd catalysts also showed the catalytic activity at 40°C, resulting from single Pd atoms as suggested by previous literature.[6] These results demonstrated that our carbonyl surface modification method can serve as a general tool to synthesize noble metal catalysts from single atom sites to sub-nano clusters.

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Metal Oxide-based Electrocatalyst for CO_2 Electroreduction – Investigating the Catalytic Surface via Pourbaix diagrams

Raju Lipin[1] , Matthias Vandichel[1*]
[1]*Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland*
[*]*Matthias.Vandichel@ul.ie*

Keywords: CO_2 Reduction, DFT, Pourbaix Diagram, NiO_x, SnO_2

Introduction. Electrocatalytic carbon dioxide reduction reactions (CO_2RR) have gained much attention in the recent years due to the significant role they play in creating clean energy.[1,2] The search for finding alternatives for the use of toxic and expensive transition metal based electrocatalysts is still an active focus in research. Recently, several studies have reported that metal oxide electrocatalysts show high CO_2RR performance.[2] In particular, SnO_2 is one of the most promising electrocatalysts for the generation of formate, however, due to the relative low intrinsic electrical conductivity its performance towards CO_2RR is far from satisfactory.[3] In this work, inspired by the experimental studies on a NiO_x:SnO_2 based electrocatalyst for CO_2 reduction to formate, a detailed molecular level understanding of the active surface of the earth abundant metal (eg. Ni) doped SnO_2 systems during the electrochemical conditions is investigated by ab initio thermodynamics employing DFT.

Experimental/methodology. Spin polarized Density functional Theory (DFT) calculations were performed with the plane wave package Vienna Ab initio Simulation Package (VASP).

Results and discussion. At electrochemical conditions, the catalytic surfaces on SnO_2 tends to get hydroxylated, and thereby altering the active terminations. Constructing surface Pourbaix diagram (SPD) based on molecular systems with various degrees of hydrogenation have aided in revealing the thermodynamically favourable terminations as a function of pH and potential.[4,5] (**Figure 1**)

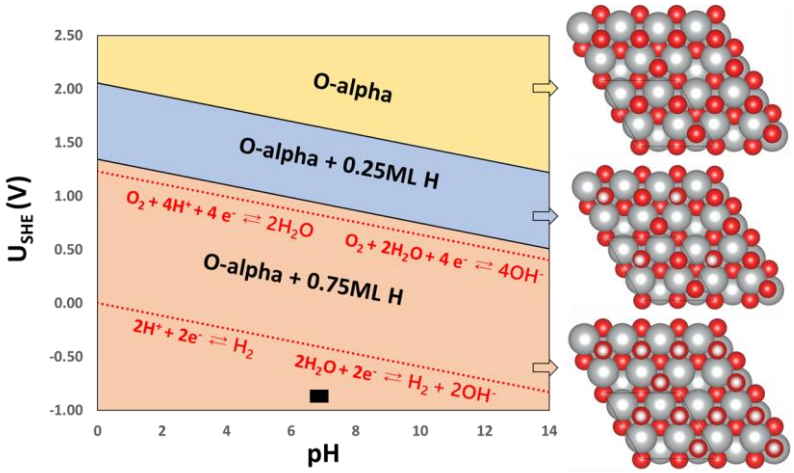

Figure 1. A representative Pourbaix diagram for a defective NiO(111) surface showing the stable terminations for a metal oxide-based electrocatalyst.[5]

Acknowledgments
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Water dynamics and p-cresol co-adsorption in (alumino)silicate CAN zeolite from machine learning potentials and DFT

D. Nováková [1*], A. Erlebach[1], L. Grajciar[1]

[1]*Charles University, Prague, Czech Republic*
[*]*denisa.novakova@natur.cuni.cz*

Keywords: Molecular dynamics, Machine learning, CAN, p-cresol

Introduction: Zeolites are traditionally used materials in the petrochemical and chemical industry that have recently drawn attention for their possible utilization in biomedicine as drug and gene carriers, materials in bone tissue engineering, or adsorbents for detoxifying human organisms.[1] Zeolites offer a possible solution for removing protein-binding uremic toxins, such as p-cresol, that are unremovable during classical hemodialysis.[2,3] This study focuses on analyzing the motion of water within zeolite with CAN framework topology using molecular dynamics (MD) simulations with neural network potentials (NNPs).[4] The obtained data is used to calculate the self-diffusion coefficients and analyze the effect of water loading, aluminum content, and the distribution of aluminum atoms on water diffusion and degree of deprotonation of Brønsted acid sites (BASs). In addition, the thoroughly tested water-loaded CAN models are used for evaluation of the interaction between the zeolite framework, water molecules and p-cresol.

Experimental/methodology: Models with CAN framework topology, various water content, Si/Al ratio and distribution of aluminium atoms were used in MD simulations performed for a time interval of 1 ns using the canonical NVT ensemble with the time step of 0.5 fs and constant temperature of 350 K. The NNPs utilized in MD simulations were constructed using the SchNetPack library. The training and testing of NNPs was accomplished by using the reference DFT data at the meta-GGA exchange-correlation functional level (SCAN+D3(BJ)). In addition, using DFT-only we studied the interaction of p-cresol and water with CAN models with different aluminum and water content.

Results and discussion: By calculating the water self-diffusion coefficients, it was ascertained that at low water loadings and low aluminum content, no diffusion is observed. At higher water loading, the molecules form clusters of two to three molecules capable of jumping a longer distance, e.g., to the neighboring BASs. At low Si/Al ratios, the water mobility is obstructed by BAS protons resulting in decreasing diffusion coefficients with higher aluminum content. Regarding BAS solvation dynamics, it was demonstrated that to completely deprotonate BAS, at least two to three protons are necessary. Also, we observed that proton solvation decreases with aluminum content and low water loading. During the simulations, almost in all systems we observed unusual *pinned* hydroxonium species[5] being formed over a 6-ring of ***can*** cage and connected to the framework oxygens by short hydrogen bonds. Lastly, the interaction between BAS and water was found to be clearly preferable over the one with p-cresol, although with higher water content, the difference between these interaction energies decreased regardless of the aluminum content. Importantly, all aluminosilicates appear to be better adsorbents of p-cresol than purely siliceous zeolite, even if p-cresol does not adsorb directly on BAS.

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A systematic computational exploration of bimetallicity and mechanical strain concepts for N_2 activation

Omer Elmutasim, and Kyriaki Polychronopoulou*

Khalifa University of Science and Technology & Center for Catalysis and Separations, Abu Dhabi, United Arab Emirates;

**Corresponding Author's E-mail address: kyriaki.polychrono@ku.ac.ae*

Keywords: nitrogen activation, ammonia production, mechanical strain, bimetallic alloys.

Introduction. The Haber-Bosch (HB) reaction is definitely one of the most important reaction of the 20th century with tremendous impact on significant, for mankind, sectors, such as fertilizers, chemical industry, medicine, bio-fuels and ammonia production [1]. It is now well accepted that the relative activity of metallic HB catalysts can be correlated to their binding energies with N-containing species in terms of a volcano-shaped relationship. Metals that bind nitrogen too strongly or too weakly are on either side of the volcano [2]. Thus, it is important to devise a *knowledge-based catalyst design* that could potentially replace the Haber-Bosch method, while achieving high efficiency and energy saving towards sustainable NH_3 production under ambient conditions. In this regard, herein density functional theory (DFT) calculations are used in order to screen the N_2 activation capacity and the accompanied electronic interactions for a portfolio of bimetallic alloys based on Mo, Ru and Fe metals, while using those metals *as reference ones*.

Experimental/methodology. Density functional theory (DFT) computations were carried out utilizing Quantum ESPRESSO package and projected augmented wave (PAW) method, using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional based on the generalized gradient approximation (GGA). The DFT-D3 method was employed for Van der Waals dispersion corrections.

Results and discussion. In this work, DFT computations are performed for Mo(110), Fe(110) and stepped Ru(0001) surfaces alloyed with wide range of TM hetero-atoms (Ni, Co, Ru, Fe, Mo, Rh, Au, Ag, Pd, Pt, and Cu) to understand the N_2 activation and dissociation steps; the monometallic surfaces are also considered as references. To begin with, the energetic stability of binary metal alloy surfaces was investigated using the formation energy as major descriptor. Overall, TM-decorated Fe alloys exhibited relatively higher stability as compared to TM/Mo(110) and TM/st.Ru(0001) surfaces. Then, the adsorption of N_2 molecule on bare metal and bimetallic (alloy) surfaces was carefully investigated with the analysis of adsorption energetics. The results revealed that the most favorable N2 adsorption conformations on the three types of alloy systems are Ru/Mo(110), Mo/Fe(110) and Mo/st.Ru(0001). The analyses of electronic characteristics (PDOS and charge transfer) revealed that high N_2 activation on these bimetallic surfaces was mainly due to the hybridization between the host and TM solute orbitals. This hybridization gave rise to considerable charge transfer from the surface to the anti-bonding orbital of nitrogen, which further weakened the triple bond and thereby promoted N_2 decoupling. The dissociation barrier for N_2 on monometallic and bimetallic substrates was also computed. It was found that all Mo-alloys, except for TM/Mo(110) (TM=Ru and Fe) surfaces, presented energy barriers lower than that of the bare Mo(110) surface. Interestingly, apart from Mo, the favorability of N2 dissociation increased while moving from the Fe(110) substrate alloying with early to late transition metal series. The origin of difference in activity of the considered Fe-based alloys can be attributed to the electronegativity difference between Fe and TM, which in turn play a pivotal role in fluctuating d-band center belong to the surface atoms. Notably, the promotion of st.Ru(0001) with TM atoms has appreciably affected the thermodynamics of dissociation process rather than the reaction kinetics. For most of the alloy surfaces studied, apart from Mo/Fe(110) one, the N2 binding energy on the previously mentioned surfaces vary as a linear function of the applied strain. This work not only introduces efficient catalysts for nitrogen activation but also provides valuable insights on the rational design of bimetallic catalysts to enhance the performance of Haber-Bosch process for NH_3 production.

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Catalytic Materials Screening by First-Principles and Machine Learning: A case of CO_2 utilization

Supareak PRASERTHDAM[1*], Piyasan PRASERTHDAM[1]

[1]*Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330 Thailand*

[*]*supareak.p@chula.ac.th*

Keywords: Density Functional Theory, Artificial Neural Network, Dry Reforming Reaction of Methane

Introduction. This work demonstrated the improved algorithm based on first-principles and machine learning techniques: density functional theory (DFT) and artificial neural network (ANN). This algorithm is a two-step procedure that comprises catalyst identification and optimization. The Ratings concept was employed to identify the catalyst's reactivity and stability. Each catalyst is given a unique index based on its activation energy obtained from DFT on (1) reactants activation (CH_4 and CO_2) and (2) coke formation and removal benchmarking to the reference catalyst: Ni(111). These indexes on the reactivity and stability surface are used to predict DRM and coking rates at specified operating conditions. Also, the coking boundary proposed in the concept is used to determine the coke-resistant region during DRM. The next step is to generate the database for DRM and coke formation/removal rates of a chosen catalyst at different operating temperatures and CO_2/CH_4 feed ratios. This information is incorporated into the on-line optimization. Ultimately, the goal is to sustain the reaction rate of a given catalyst in the reactor and its coke-resistant property when changes in the condition of the reformer feed composition due to variations of fuel sources are present.

Experimental/methodology. Spin-polarized periodic density functional theory (DFT) calculations were employed via the Vienna ab initio simulation package (VASP). The Projector Augmented Wave pseudopotentials (PAW), plane-wave basis sets, and exchange-correlation functional described within the generalized gradient approximation (GGA) with the functional by Perdew, Burke, and Ernzerhof (PBE) were used for all systems. The Monkhorst-Pack Brillouin zone integration grid of $4\times4\times1$ with the first order Methfessel-Paxton smearing method of 0.2 eV smearing width was used. The convergence criteria are 10^{-4} and 10^{-3} eV for successive electronic and ionic steps. The climbing method nudged elastic band (CI-NEB) was employed to obtain each elementary step's activation energy (Ea). For the Ni oxide, the Hubbard-U correction was used with the GGA-PBE functional with U_{eff} used at 5.4 eV. The assumptions and simplifications of the DRM mechanism were reported in our previous works[4], where the surface reaction is the rate-limiting step. The zero-point energy (ZPE), entropy (S), and internal energy (U) contributions were considered. The pseudo-steady-state hypothesis (PSSH) was applied to determine surface coverages, with no "most abundant reactive surface species" (mari). The $CO_{(g)}$ and $H_{2(g)}$ are assumed to be in the adsorption-desorption equilibrium. Reactivity and stability were illustrated via DRM rate and coke formation from CH and CO and coke removal via H and O, respectively, at a reaction condition of 1000 K with a unity CO_2/CH_4 feed ratio.

Results and discussion. It was demonstrated that the reaction would rapidly proceed on the carbide $Ni_3C(001)$ and the metallic Ni(111) surfaces but would be suppressed on the oxide surface of NiO(100) and the metallic Ni(100) due to the presence of high E_a. Hence, a reactive and stable DRM catalyst would need to be oxide-dominated on the (100) while being metallic-dominated on the (111) facet. On the DRM reactivity, all of the metallic, oxide, and carbide surfaces are active, except NiO(100). Hence, the surface composition that yields reactive and stable Ni-based DRM catalysts is proposed to have less than 10 % of carbide, and up to 75 % metallic is needed.

Acknowledgments

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Mechanistic insights on the catalytic hydrogenation of furfural derivatives on Pd and Ru surfaces

M. Quayle,[1] M. Pera-Titus,[1] A. Roldan[1,*]

[1]*Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT*
[*] *roldanmartineza@cardiff.ac.uk*

Keywords: Hydrogenation, furfural derivates, heterogeneous catalysis, biomass, DFT.

Introduction. As industry moves towards a circular economy of chemicals, it is imperative that green catalytic processes are developed to reduce humanity's reliance on unrenewable feedstocks. Furfural and its derivates are furanic aldehydes that can be cheaply extracted from food waste,[1,2] and have shown promise as renewable reagents in organic synthesis.[3,4] With the proper use of heterogeneous catalysts, furfural derivatives can undergo hydrogenation to provide synthetic chemists with a wide variety of useful precursors.[5,6]

Methodology. The mechanism behind the catalytic hydrogenation of furfural derivatives on Pd(111) and Ru(0001) was investigated by constructing spin-polarized density functional theory (DFT) periodic models for each of the possible hydrogenation sites. The exchange-correlation contributions were calculated within the constraints of the generalized gradient approximation (GGA) using the revised Perdew-Burke-Ernzerhof (RPBE) functional.[7] Transition states were modelled using improved dimer methods and confirmed by a single imaginary vibrational mode along the reaction coordinate.[8–10]

Results and discussion. Herein, we report novel insights into how furfural-based unsaturated ketones bind to these metal catalysts through their ring systems and carbonyl groups. In agreement with experiment,[4] hydrogenation of α,β-double bonds on the carbon chain (Figure 1) is energetically preferred over hydrogenating the ring system on both Pd and Ru, but Pd hydrogenation proved to be more selective. On Pd, the substrate favored strong interactions with the furan ring, whereas Ru catalysis was dominated by the oxophilicity of the surface, prioritizing interactions with the carbonyl and ring oxygens. We also highlight the role that C=C conjugation plays in stabilizing ring hydrogenation intermediates.

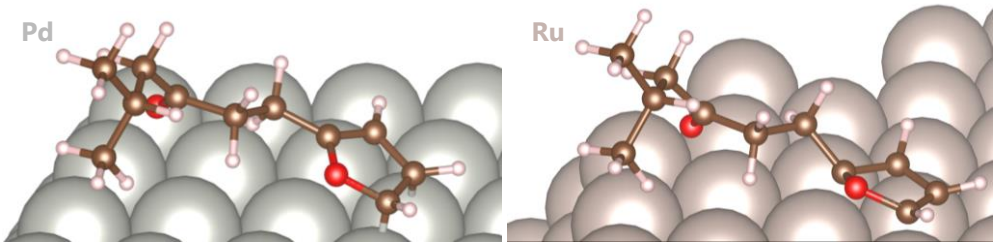

Figure 1. Furfural derivatives on Pd(111) (left) and Ru(0001) (right) after the hydrogenation of the α,β-double bond.

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Rate Determining Steps and Development of Rate Equation for Oxidative Dry Reforming of Methane over Supported Ni Catalyst

A. S. Russel[1], Satyam Gupta[1], Goutam Deo[1,2*]
[1]*Department of Chemical Engineering, Indian Institute of Technology, Kanpur, India*
[2]*Department of Sustainable Energy Engineering, Indian Institute of Technology, Kanpur, India*
[*]*goutam@iitk.ac.in*

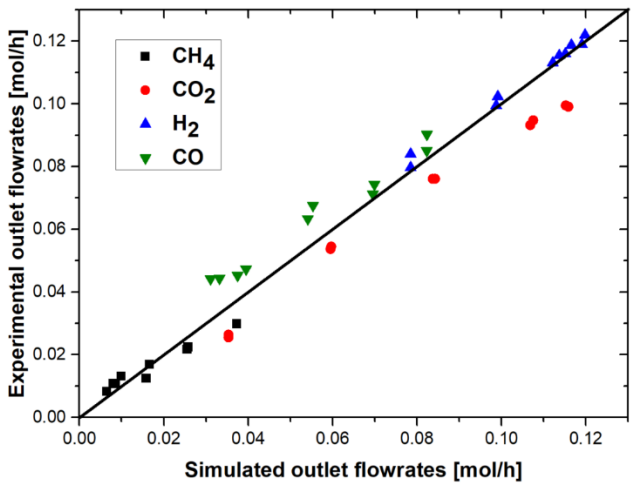
Keywords: Microkinetic modelling, oxidative dry reforming, rate-determining step

Introduction:
Dry reforming of methane (DRM), utilising CO_2 and CH_4, is increasingly being considered as an alternative to produce H_2 and syngas (a mixture of H_2 and CO). The DRM with O_2 co-feed reaction, also called oxidative dry reforming of methane (ODRM), produces more H_2 at milder than the DRM reaction conditions. One way to represent ODRM is given in reaction 1. In analysing reaction kinetics involving complex reaction mechanisms, the evaluation of the rate-determining step (RDS) has proven to be very useful. However, there is a lack of agreement regarding the RDS of DRM, which is necessary for the understanding of the ODRM reaction. Furthermore, the RDS can assist in developing an appropriate rate equation. Microkinetic models (mkm) play a crucial role in addressing these knowledge gaps.[1]

$$CH_4 + CO_2 + 0.5O_2 \rightarrow 3CO + 4H_2 \quad (1)$$

Experimental/methodology:
In this study we use various O_2 feed rates to conduct the ODRM reaction over a freshly prepared alumina-supported Ni catalyst. The incipient wet impregnation approach was used to synthesised the 15% w/w Ni supported on Al_2O_3 catalyst. The steady state concentration of all the surface species is calculated by mkm, where a set of differential equations and site balance are solved. The rates are incorporated into the continuity and species balance equations and solved to determine the molar flow rates of the gaseous species along the axial distance of the reactor. An existing general reforming reaction mechanism for ODRM over an alumina-supported Ni catalyst is used for developing the mkm.[2] Validation is achieved by comparing experimental and mkm-calculated outlet flow rates at different feed rates of O_2 and two contact times.

Results and discussion:



The mkm using the existing 52 steps reaction mechanism is successfully validated as shown in Figure 1. We then proceed to identify the RDS(s) through a hierarchical strategy using sensitivity analysis for the varying amounts of O_2 co-feed.[3] After identifying the RDS(s), we derive an overall rate equation that effectively simulates the DRM reaction with different O_2 co-feed amounts. We then examine the effect of O_2 co-feed amounts on the hydrogen yield and ascertained the presence of a maximum in hydrogen yield. Thus, mkm proves very helpful in developing suitable rate equations and analysing the ODRM reaction.

Figure 1: Comparison between mkm results and experimental data

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Theoretical study of local and global deformation of H-ZSM-5

A.Seremak[1*], T. Fjermestad[1], S. Svelle[1]

[1]*Center for Materials Science and Nanotechnology (SMN), Department of Chemistry, University of Oslo, Oslo, Norway*

[*]*agnieszka.seremak@kjemi.uio.no*

Keywords: H-ZSM-5, zeolite, Brønsted acid sites, DFT

Introduction. H-ZSM-5 is a widely studied zeolite catalyst used commonly in the metanol-to-hydrocarbons (MTH) reaction. Its topology is characterized by a 3D cross-linked pore system, formed by sinusoidal (along the *a* direction) and straight (along the *b* direction) channels. One of the main limitations of this zeolite is the loss of catalytic performance when nonreactive species *i.e.*, coke, accumulates.[1] In a recent study, the structural distortions of H-ZSM-5 zeolite have been monitored by *operando* time-resolved synchrotron X-ray diffraction.[2] It was observed that the presence of coke species affects the architecture of the straight channel, distorting it to an elliptical-like shape. Xiong *et al.* also reported the same behavior in a study of ZSM-5 with benzene as probe molecule using in situ STEM.[3]

In the present work we explore the sensitivity of the zeolite to adsorbed species at a detailed atomistic level. Particular attention is given to the effect of Brønsted acid (BA) site position and the type of coke molecules on the local (represented by the deformation of pore shape) and global (described with previously introduced "a-b" parameter) structural changes. This work will shed light on the fundamental properties of zeolites and their deactivation behavior, while aiding in the interpretation of experimental results.

Experimental/methodology. Periodic density functional theory using the plane wave basis set and Gaussian ortbital scheme method is applied to model the influence of different hydrocarbon guest species and the effect of Al position on global and local structural distortion in H-ZSM-5. The calculations are executed with PBE exchange correlation functional and a plane-wave auxilary basis set cutoff at 660 Ry.

The investigated MFI zeolite structure model has Si/Al ratio of 31. Three different active sites are investigated and hydrocarbons are placed in either the intersection, straight or sinusoidal channel. The guest species are placed in the zeolite pores in a stepwise manner – up to 4 molecules per cell, and the system relaxation is performed.

Results and discussion. Our calculations revealed that all examined hydrocarbons prefered the easily available channel intersection. This is in agreement with the previously reported work.[4] To quantify the pore distortion, we measured the distance between two opposite T-atoms of the straight channel and calculated the aspect ratio using the longest and shortest distances.

We observe that independent of the type of coke species, there exists a relationship between the BA site position and the local structural distortion, i.e. when guest species has low accessibility to the proton, the pore shape changes are the most noticeable. Furthermore, depending on the type of adsorbed molecule we can recognize two types of behavior. Upon one-by-one aromatic hydrocarbon insertion, the unit cell shrinks in the *a* direction, resulting in the decrease of the "a-b" parameter. The size of the cell along *b* and *c* directions are not affected by these compounds. The second type of behavior can be linked to methylated benzenes. Regardless of proton siting, coke occupation of the pores leads to cell expansion in the *b* direction and moderate contraction in the *a* direction, resulting in "a-b" parameter reaching values close to zero. This study presents a non-indentical structural behavior of H-ZSM-5 depending on the active site location and type of coke compound.

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Computational views on Copper Dimer

Dmitry Sharapa[1*], Karin Fink[2], Christof Wöll[3], Felix Studt[1,4]

[1]*Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT)*
[2] *Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT)*
[3] *Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT)*
[1,2,3] *Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany*
[4] *Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Engesserstr. 18 / 20, 76131, Karlsruhe, Germany*
[*]*dmitry.sharapa@kit.edu*

Keywords: MOF, HKUST-1, computational catalysis, multireference, adsorption, CO-oxidation

Introduction. HKUST-1 is one of the first synthsised MOFs, as well as one of rare MOFs with coordinatively unsaturated metal centers, it is also relatively robust, has high porosity and crystalinity. This braught a lot of attention to this material over years, yet, there is many puzzles to be solved. Here we would like to focus on three different aspects of paddle-wheel (PW) copper center: adsorption on the ideal PW, catalytic oxidation on defective PW and water-induced colour change of HKUST-1. All three studies are complicated by multireference nature of studied objects.

Methodology.
"Adsorption" project:
PBE, B3LYP, M06–L, BEEF–vdW, as well as CASSCF, NEVPT2, DLPNO-MR-CCSD with 2x2 active space.
"Catalysis" project:
M06 + CASSCF/NEVPT2 with 5x4 active space
"Spectroscopic" project:
CIS, TDA and TD-DFT with different functionals, CASSCF, NEVPT2, SORCI and MRDDCI3

Results and discussion.

"Adsorption". Although DFT approaches are not properly accounting multiconfigurational nature of ground state of PW, they appears to be able to describe adsorption relatively good. We showed out that CASSCF strongly underestimate and NEVPT2 overestimate binding energies. These drawbacks are properly accounted in DLPNO-MR-CCSD that is extremely accurate, but its ultimative cost strongly hinder its application.[1]

"Catalysis". We showed out that pristine PW cannot catalyse CO-oxidation, and the process take place on "linker-missing" defects, where Langmuir-Hinshelwood reaction between CO and O_2 results in formation of an intermediate that is then broken by second CO molecule. While mechanism can be built with DFT-approaches, found barrier would not allow process to take place under low-temperature conditions. Reason of it lies in multireference nature of Transition State (TS) that unify two single-referent intermediates. Proper treatment of this TS results in a barriers that are in excellent agreament with experimental conditions. Defect-driven mechanism suggested by computations was confirmed experimentally.[2]

"Spectroscopy". Hunt on mysterious colour change of HKUST-1 drove us to the system, excitations of which (despite looking very simple) can't be reliably described by typical approaches. Approaches of outstanding cost and complexity were used for nailing down the peaks.

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Ru nanoparticles modelling and simulation for ammonia synthesis

Luka Skubic[1, 2*], Sašo Gyergyek[1], Blaž Likozar[3], Matej Huš[3]

[1]*Jožef Stefan Institute, Ljubljana, Slovenia*
[2]*University of Maribor, Faculty of chemistry and Chemical Engineering, Maribor, Slovenia*
[3]*National Institute of Chemistry, Ljubljana, Slovenia*
[*]*luka.skubic@ijs.si*

Keywords: Ammonia synthesis, DFT calculations, Ru nanoparticles

Introduction. Ammonia has a big impact on our lives since it is mostly used for the production of fertilizers, which are necessary to grow crops. Ammonia is produced via the Haber–Bosch (HB) process, which is more than 100 year old but still most commonly used for ammonia production.[1] Due to major drawbacks of the HB process, such as a high energy consumption (more than 2 % of global energy is used only for ammonia production) and CO_2 emissions, new ways of ammonia synthesis are investigated, where different types of catalysis would be used. [1,2] A lot of effort is being put into the catalyst design using experimental as well as theoretical approaches. First principles calculations and microkinetic modelling are used to predict the catalyst shape and structure, investigate reaction mechanism, computational fluid dynamics are used for reactor design. [3]

Experimental/methodology. Using DFT calculations, we are modelling a Ru catalyst for ammonia synthesis. For the purpose of our symulations, we used the GPAW software where the wave functions were described with plane waves (PW) with a cut-off energy of 450 eV and a 2x2x1 k-point mesh. The dispersion correction DFT-D3 and dipole correction were applied to our calculations. NEB calculations with the climbing image approach were used to find transition states and activation barriers. The DFT results were used in microkinetic modelling.

Results and discussion. First-principles calculations allowed us to calculate favourable adsorption sites for the single atom as well as the molecular adsorption over Ru(0001) slab. We studied 6 possible adsorption sites for N_2 adsorprtion. Lattice size manipulation allowed us to model entire dissociative mechanism for ammonia production and to create relations between the activation barrier and adsorption energies for further Ru nanoparticles modelling. We have modelled simple Ru nanoparticles and researched different edges, planes and vertices in order to find the most favourable Ru shape for ammonia production.



Figure 11: Ammonia synthesis mechanism over Ru (0001).

Acknowledgments
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Predicting Adsorption Energies on Bimetallic Cu-based Catalysts via ML

A. Usuga[1*], A. Comas-Vives[1,2]

[1]*Department of Chemistry, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Catalonia, Spain.*
[2]*Institute of Materials Chemistry, TU Wien, 1060 Vienna, Austria.*
[*]*Email: andresfelipe.usuga@uab.cat*

Keywords: DFT, Machine Learning, bimetallic alloys, adsorption energy.

Introduction. Increasing the performance of heterogeneous catalysts is challenging. To predict better materials for tailored reactions, it is a fundamental step to relate the nature of catalysts and their catalytic activity. Theoretical studies allow screening at a lower cost compared to experiments. Adsorption energies of reactive intermediates are a key catalytic descriptor, as one can relate them to the catalytic activity. Nevertheless, the calculation of adsorption energies is costly and increases with the number of reaction intermediates, facets and the complexity of the evaluated materials. For instance, in the case of bimetallic alloys, the adsorption energies of catalytic intermediates are not easily predictable since they do not follow a linear trend among adsorbates of the same family. Thus, machine learning (ML) algorithms have arisen as an alternative to predict adsorption energies on monometallic surfaces [1]. Still, they must be redesigned to predict the adsorption energies of bimetallic alloys.

Experimental/methodology. The present work focuses on built-up a workflow to generate a database; this database will be used to train an ML-based model to predict the adsorption energy on bimetallic alloys. We first design a workflow to generate the database for different facets of Cu-based alloys: the generation of each bulk structure, the bulk optimization to get its lattice parameter used to build the slab, the relaxation of the clean alloy surface, and adding the adsorbate on it, and finally, reoptimize the resulting structure to obtain its adsorption energy. Currently, we are working on aspects related to the parameters of the ML-based model; we are developing and testing features of both the clean surface and the adsorbate.

Results and discussion. With the development workflow to generate the database, we got several surface models using FCC bulk structures. Some effects were included in the ML model to increase their robustness; the following list contains the studied aspects: the facet, possible slab termination, chemical composition, and type of adsorption site. Additionally, we use features that only require calculating properties for the clean surface and insulated adsorbate, such as Bader charges, occupancies, electronegativities, and coordination numbers. With the current model based on the XGBoost ML algorithm, we obtain a model with an MSE of 0.012 and 0.307 eV for the train and test sets, respectively. The current ML model shows that it is possible to predict the adsorption energy in complex systems such as bimetallic alloys.

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CO_2-ZrO_2 Interaction in CDRM: A Combined Experimental and Theoretical Study

A. Uzun[1,2,3], A. I. Paksoy[1], B. S. Caglayan[2,3], A. E. Aksoylu[1,2*]

[1]*Department of Chemical Engineering, Boğaziçi University, Bebek, Istanbul 34342, Turkey*
[2]*SNG&HydTec Lab, Science and Technology Building, Boğaziçi University, Kandilli, Istanbul 34684, Turkey*
[3]*Advanced Technologies R&D Center, Boğaziçi University, Bebek, Istanbul 34342, Turkey*
[*]*aksoylu@boun.edu.tr*

Keywords: m-ZrO_2, FTIR-DRIFTS, DFT, XPS, CO_2 adsorption, O migration

Introduction. Stable CDRM performance of a catalyst is dominantly determined by its ability to dissociate CO_2 to produce and utilize surface oxygen at rates high enough to clean surface carbon formed on its active sites. The current study is an attempt to understand the nature of CO_2 activation on a commercial ZrO_2, which is a widely used CDRM support responsible for CO_2 dissociation and surface O mobility, via combined evaluation of computational and experimental findings.

Experimental. Calcined and reduced ZrO_2 (from Alfa Aesar), ground to 45-60 mesh size, was characterized by using a XRD and XPS. The FTIR-DRIFTS analysis was performed on a Bruker Vertex 70V equipped with an MCT detector, and DRIFTS cell with ZnSe window. The spectra were collected at a resolution of 4 cm^{-1} and 128 scans. The samples prepared in powder form were blended with KBr in 1 to 5 ratio. CO_2 adsorption tests were carried out with 10% CO_2-He mixture at RT, 373 K and 573 K for 30 min and the mixture was flushed with pure He flow for 30 min afterwards.

Computational. Spin-polarized DFT calculations were performed for repeated slab geometry, by using the program package CASTEP in Materials Studio. Exchange and correlation were included through the use of GGA-PBE functional. m-$ZrO_2(\bar{1}11)$ surfaces were modeled as a two-layer slab with 14 Å vacuum thickness. Adsorption of CO_2, CO and O was studied on (1x1) surface unit cell. Adsorption energies were calculated. Local density of states (LDOS) analysis was performed. The energy barrier for an oxygen atom moving from one stable site to another was calculated by the CASTEP Transition State Search Task.

Results and discussion. The XRD spectrum showed peaks corresponding to characteristic reflection planes of monoclinic zirconia (JCPDS 86-1449). FTIR-DRIFTS analyses of CO_2 adsorption on m-ZrO_2 samples at different temperatures confirmed CO_2 activation and ZrO_2-CO_2 interaction via detection of surface bicarbonate, carbonate, formate and OH species as well as bridged CO (Figure 1). It was also shown that the extent of the interaction is very much related to temperature; reversible formate formation pathway is found to dominate at 573 K. XPS analysis results revealed the existence of oxygen vacancies and defect sites. DFT simulations of CO_2 adsorption revealed that bidentate and tridentate carbonates are formed while dissociative CO_2 adsorption does not take place on m-$ZrO_2(\bar{1}11)$ surface. The lower energy barrier for oxygen mobility between sites A, B, C and D which is below ca. 1.0 eV enables higher oxygen mobility on these sites (Figure 2). High oxygen mobility on ZrO_2 surface allows O migration from ZrO_2 support to the catalyst active metal sites suffering from surface carbon deposition. Combined evaluation of experimental and computational results hints that O-defect on m-ZrO_2 are necessary for CO_2 siplitting.

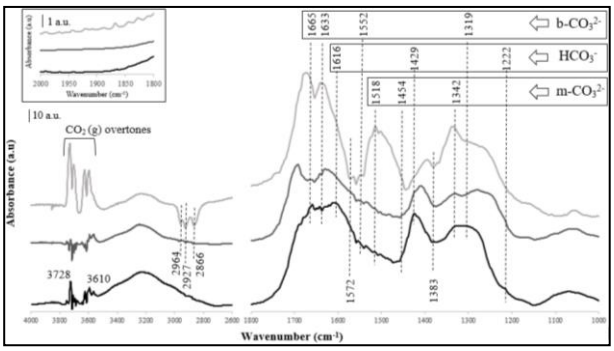

Figure 1. FTIR-DRIFT spectra obtained on ZrO_2 after He flush of 10% CO_2 adsorption at RT(bottom), 373 K and 573 K (top).

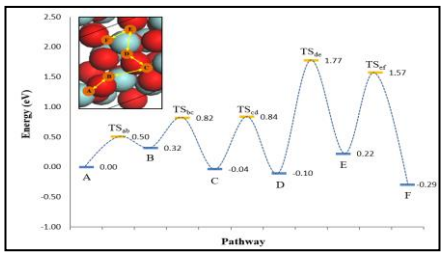

Figure 2. Potential energy profile for oxygen mobility pathway on m-r$O_2(\bar{1}11)$ surface.

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Elucidation of Structure–Activity Relations in Electrocatalytic Hydrogen Evolution Reaction at Pd Hydride Surfaces: Theoretical Insight

A. Ngoipala, R. Lipin, R. L. Arevalo, M. Vandichel*

Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick, V94 T9PX, Ireland
**matthias.vandichel@ul.ie*

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Introduction. The structure–activity relationship is a cornerstone topic in catalysis, which lays the foundation for the design and functionalization of catalytic materials. Of particular interest is the catalysis of the hydrogen evolution reaction (HER) by palladium (Pd), which is envisioned to play a major role in realizing a hydrogen-based economy. Interestingly, experimentalists observed excess heat generation in such systems, which became known as the debated "cold fusion" phenomenon.[1-3] Despite the considerable attention on this report, more fundamental knowledge, such as the impact of the hydride formation on the stability of Pd hydride structures and HER activity, remains largely unexplored.

Experimental/methodology. In this work, first-principles density functional theory calculations were carried out to characterize the adsorption and absorption behaviors of hydrogen on Pd surfaces, directing a particular focus on the stability and HER activity of model Pd hydride surfaces.

Results and discussion. Our computational results reveal that among the low-indexed surface planes for an fcc Pd, the (111) surface is not only expected to be the most dominant surface in a Pd nanostructure, but also the most preferred surface for hydrogen adsorption. The calculated surface energies indicate the greater stability of the surfaces containing hydrogen subsurfaces over the corresponding clean ones (Table 1). Under electrochemical conditions, the calculated Pourbaix diagrams show that below the equilibrium potential and pH region at which HER can take place, Pd surfaces are already covered by hydrogen adatoms. In addition, the thermodynamically most stable systems contain more and more Pd hydride subsurface layers when decreasing electrode potential. Interestingly, the formation of subsurface hydride results in a compressive strain, which lowers the H adsorption free energy on (111), (110), (100), and (211) facets, thereby increasing the HER activities. In the presence of strain, the HER activities in the model surfaces were in the decreasing order of (211) > (111) > (110) > (100), in agreement with the experimental results.[4] These findings provide significant insights into the role of subsurface hydride formation on the structure–activity relations toward the design of efficient Pd-based nanocatalysts for the HER.

Table 1. Calculated surface energy of Pd(111), (100), (110), and (211) surfaces containing different numbers of PdH sublayers.

Number of PdH sublayers	Surface energy (γ)*, eV/Å^2			
	Pd(111)	Pd(100)	Pd(110)	Pd(211)
0	0.132	0.145	0.150	0.147
1	0.092	0.112	0.124	0.103
2	0.056	0.075	0.101	0.066
3	0.031	0.047	0.079	0.033
4	0.005	0.018	0.058	0.004

* $\gamma = \gamma_{H^*_{sub}/Pd} - \gamma_{Pd,clean}$ where $\gamma_{H^*_{sub}/Pd} = \frac{1}{A}\left(E_{Pd,slab+H^*_{sub}} - \frac{N_H}{2}E_{H_2} - N_{Pd}E_{Pd_1,bulk}\right)$; $\gamma_{Pd,clean} = \frac{1}{2A}\left(E_{Pd,slab} - N_{Pd}E_{Pd_1,bulk}\right)$

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