CHIMIA

CHIMIA 2016, Volume 70
ISSN 0009-4293
www. chimia.ch

SCS
Swiss Chemical
Society

Supplementa to Issue 7-8/2016

SCS Fall Meeting 2016

Poster Abstracts
Session of Catalysis Science & Engineering

September 15, 2016
University of Zurich, Irchel Campus
http://scg.ch/fallmeeting/2016

Swiss Chemical Society
Haus der Akademien
Postfach
3001 Bern
Switzerland
info@scg.ch
www.scg.ch

Enhancing the stability of Pd catalysts for methane oxidation using hierarchical ZSM-5

A. W. Petrov[1], D. Ferri[1], O. Kröcher[1,2], J. A. van Bokhoven[1,3]*

[1]Paul Scherrer Institute, Villigen, [2]EPF Lausanne, [3]ETH Zurich

Catalytic methane oxidation is used in exhaust gas after-treatment to reduce unburnt methane emissions in stationary combustion processes and in natural gas vehicles [1].Despite their promising activity, Pd/zeolite catalysts suffer from rapid deactivation under reaction conditions especially in the presence of steam, mainly due to sintering of the active phase [2].In this work, the stability of palladium nanoparticles was increased by introducing mesopores in ZSM-5 by acid leaching. This synthesis approach enabled us to produce Pd/ZSM-5 catalysts exhibiting higher activity and improved stability in complete methane oxidation in the presence of water vapour.

ZSM-5 zeolite (Zeochem PZ-2/40, Si/Al=20) was leached with 65 wt.% nitric acid at 80°C for 4 h in reflux. Then the conventional and the dealuminated zeolite were ion-exchanged with palladium ammonium nitrate to obtain 1 wt. % palladium loading, the catalysts were dried and calcined at 500°C. Stability of the catalysts was evaluated in a quartz glass plug-flow reactor with a feed of 1 vol.% CH_4, 4 vol.% O_2 and 5 vol.% H_2O (bal. N_2) at GHSV = 80,000 h^{-1} and constant temperature (450°C).

The acid treatment led to an increase of the Si/Al ratio from 20 to 30 while argon physisorption indicated the formation of uniform super-micropores of 1.9 nm in diameter. HAADF-STEM revealed that the dealuminated catalystpossessed evenly distributed palladium nanoparticles of 1-2 nm. Because the particles are too large to be accommodated in the micropores of ZSM-5 (0.55 nm), these particles likely occupy the super-micropores generated by the acid treatment.

The conventional Pd/ZSM-5 catalyst deactivated rapidly during methane oxidation, while the dealuminated catalyst exhibited significantly higher activity and stability. We attribute the increased stability to the physical separation of the metal nanoparticles by the support, which prevents the active phase from sintering, and the higher Si/Al ratio of the dealuminated catalyst, that imparted additional stability to the zeolite structure.

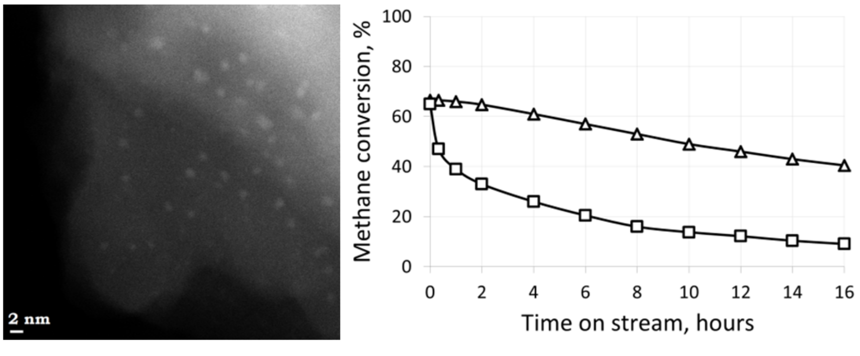


Figure 1: (a) STEM image of the catalyst based on dealuminated zeolite and (b) catalytic activity of the catalysts based on the conventional zeolite (o) and the dealuminated zeolite (r) at 450°C in the presence of 5 vol. % water

[1] P. Gelin, M. Primet, Appl. Catal. B: Environmental. 39 (2002) 1.
[2]Y. Li, J.N. Armor, Appl. Catal. B: Environmental. 3 (1993) 275.
[3] C. Descorme, P. Gelin, C. Lecuyer, M. Primet, Appl. Catal. B: Environmental 13 (1997) 185

Growth mechanism and optimization of the Co_3O_4 spinel matrix for water oxidation

L. Reith[1], K. Lienau[1], R. Moré[1], D. Cook[2], R. Walton[2], Y. Wu[3], G. R. Patzke[1]*

[1]University of Zurich, [2]University of Warwick, [3]University of Oxford

Artificial photosynthesis is a promising way for the storage of renewable energy as chemical fuels through splitting of water into oxygen and hydrogen, which can be further processed. The four electron transfer process of water oxidation remains the efficiency bottleneck and calls for the development of efficient, stable and economic water oxidation catalysts (WOCs). Spinel-type Co_3O_4 keeps attracting strong research interest as a low-cost and robust WOC.[1] The catalytic activity of this material depends on multiple parameters, such as crystallinity, oxidation states, morphology, and surface area.[2] Identifying and controlling these parameters poses a preparative and analytical challenge. Deeper insight into the growth mechanism for the Co_3O_4 is required for its rational WOC design by addressing the key performance parameters. We thus investigated nanoscale Co_3O_4-spinel type WOC growth by in-situ PXRD measurements and complementary ex-situ quenching experiments.

In order to further explore the tuning potential of this WOC, post-synthetic treatments and investigations on the influence of different transition metal combinations (Co, Ga, Fe, Ni) in the spinel matrix were carried out. Generally, catalytic activity of WOCs depends strongly on the respective evaluation protocol.[3] In this investigation, photocatalytic and electrocatalytic methods are compared to differentiate their influence on the water oxidation activity of Co_3O_4-based WOCs.

Controlling particle size distribution of nickel particles supported on γ–alumina by a molecular approach

T. Margossian[1], S. Kim[1], A. Fedorov[1], C. Copéret[1]*, C. Müller[1]*

[1]ETH Zurich

Supported nickel nanoparticle onto γ–alumina is a commonly used catalyst for several industrial reactions such as reforming[1], methanation[2] and hydrogenation reactions[3]. However, the activity of such catalyst is often limited by the low metal dispersion and a high content of unreducible metal that is obtained by conventional preparation methods in aqueous phase[4].

Here we show that $(tmeda)_2Ni_2(OCHO)_4(H_2O)$ (Figure 1-a)) can be used as a convenient nickel precursor to prepare supported metallic nanoparticles on γ–alumina. In particular, this precursor is soluble in a broad solvents (water or organic solvents) and can thus be used for the impregnation of supports in a large variety of conditions, prior to the formation of nanoparticles via reduction under H_2. Each step of the preparation process was characterized at different stages of catalyst preparation, i.e. from precursor adsorption (NMR, FTIR, UV-VIS, EXAFS) to particle formation (TEM, CO adsorption tracked by FTIR, XANES, H_2 Chemisorption).

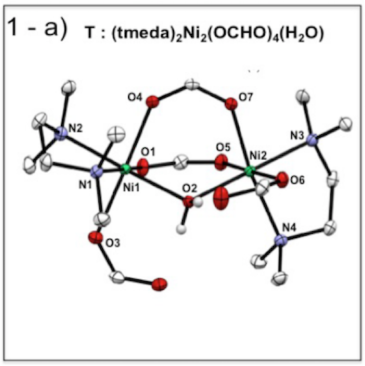


Figure 1: a) Single crystal structure of $(tmeda)_2Ni_2(OCHO)_4(H_2O)$

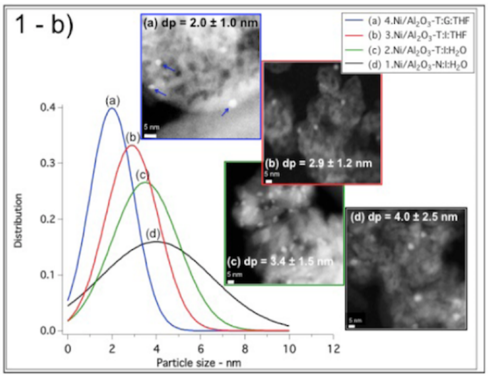


Figure 1: b) Particle distribution function of the particle size for the different catalysts, N: $Ni(NO_3)_2.6H_2O$

The grafting and control deposition reduction of the molecular precursor allows the formation of small and narrowly distributed Ni particles (2.0 ± 1.0 nm) when using organic solvent by comparison to the use of convention precursor (4.0 ± 2.5 nm by conventional impregnation of nitrate precursor in aqueous medium, Figure 1-b)). XAS clearly shows that the proportion of $NiAl_2O_4$ was also strongly diminished in the former case, thus illustrating the advantage of organic solvent and organic soluble molecular precursors. Under dry reforming of methane conditions, the smallest supported nanoparticles showed greatly enhanced initial activity, likely because of the higher metal dispersion.

[1] D.-B. Cao, Y.-W. Li, J. Wang, H. Jiao, *J. Phys. Chem. C* **2011**, *115*, 225-233.
[2] B. Mutz, H. W. P. Carvalho, S. Mangold, W. Kleist, J.-D. Grunwaldt, *J. Catal.* **2015**, *327*, 48-53.
[3] R. Molina, G. Poncelet, *J. Catal.* **2001**, *199*, 162-170.
[4] F. Négrier, E. Marceau, L. Gengembre, A. Löfberg, *J. Phys. Chem. B* **2005**, *109*, 2836-2845.

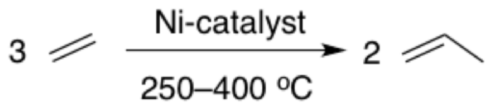
Ethene-to-Propene Conversion on Well-Defined Surface Nickel Sites

I. Moroz[1], A. Fedorov[1], C. Copéret[1]*

[1]ETH Zurich

Propene is one of the most important industrial building blocks and it is derived from petrochemicals. The demand for propene is constantly growing, which puts pressure on existing propene production processes and stimulates the development of alternative pathways. Recently a novel and highly promising technology appeared that directly converts ethylene to propene, the so-called ETP reaction. The ETP process proceeds on Ni-based heterogeneous mesoporous catalysts (Ni-MCM-41) above 400 °C [1]. Under optimized conditions ethylene conversion up to 68 % and propene selectivity up to 48% was reported [1]. Subsequent work has shown that incorporation of aluminum into Ni-MCM-41 increases the catalytic activity that reaches the optimal performance with Si/Al ratio of 60 (Scheme 1) [2].

Scheme 1. The ETP reaction on Ni sites



Literature Ni-catalysts: Ni-MCM-41 [1], Ni-(Al)MCM-41 [2]

This work: Ni/support (single sites via molecular chemistry)

Despite years of research [3-5], the nature of the active sites as well as the underlying reaction mechanism are not proven. Here, we describe the synthesis of well-defined Ni surface sites with known oxidation state and nuclearity at the surface of oxide materials via the controlled grafting and subsequent thermolysis of well-defined nickel molecular precursors. This approach paves the way to understand the key elementary steps of the ETP reaction on Ni sites.

[1] M. Iwamoto, Y. Kosugi, *J. Phys. Chem. C* **2007**, *111*, 13.
[2] L. Alvarado Perea, T. Wolff, P. Veit, L. Hilfert, F.T. Edelmann, C. Hamel, A. Seidel-Morgenstern, *J. Catal.* **2013**, *305*, 154.
[3] M. Iwamoto, *Catal. Surv. Asia* **2008**, *12*, 28
[4] M. Iwamoto, *Molecules* **2011**, *16*, 7844
[5] M. Iwamoto, *Catal. Today* **2015**, *242*, 243

Microbial fuel cell triple stack characteristics

M. Sugnaux[1], C. Savy[2], G. Huguenin[2], F. Fischer[1]*

[1]HES-SO Valais, [2]HE-Arc

Microbial fuel cells (MFCs) are thought to become in a near future a way to directly convert organic matter into electrical energy [1]. Such bioelectrical systems, are intended to become integrated in wastewater treatment plants. The current challenge is the scale-up of these devices [2].

Stacked MFCs in serial connection could increase the performance of such systems. A three unit MFC was designed and built at the HES-SO Valais (Fig. 1). Polarization experiments were realized to assess the behavior of the individual units in the stack as well as the whole stack. As previously described in the literature [3], the voltage reversal phenomenon (Fig. 2) decreases the performance of such stacks. The origin of these voltage reversals was investigated and solutions elaborated to solve the problem.

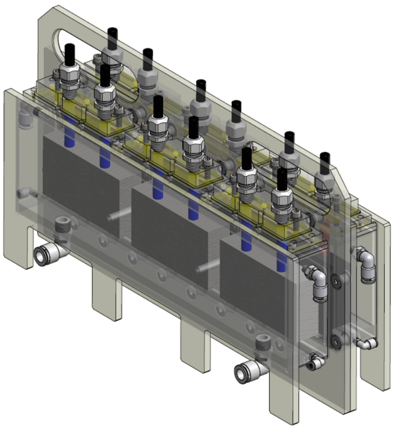


Figure 1 : Microbial fuel cell triple stack

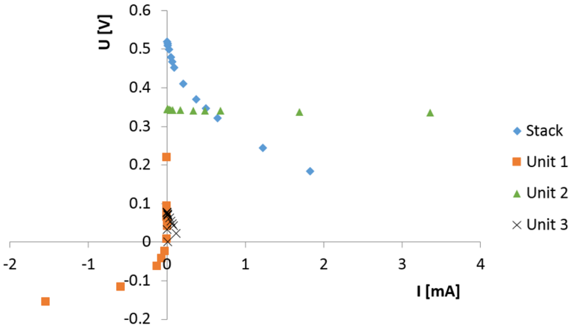


Figure 2 : Polarization curve

At first maximum power produced with the stack treating synthetic urine was 0.24 mW/m^2. The performance of the stacked MFC increased up to 2.7 mW/m^2 when the unit presenting voltage reversal was isolated from the stack. It was shown that the phenomenon was linked to biofilm development on the anode through electrodes permutation experiments and biofilm analysis. Voltage reversal on defective unit was eliminated when electrical circuit was alternated, maximum power of the stack was then 7.1 mW/m^2. The objective of the project is scale-up, the next step is larger12 units MFC.

[1] Prashant Pandey, *Applied Energy*, **2016**, 168, 706-723.
[2] Anil N. Ghadge, *Bioresource Technology*, **2015**, 182, 373-377.
[3] S.-E. Oh, *Journal of Power Sources*, **2007**, 167, 11-17.

Modeling of Sustainable Base Production by Microbial Electrolysis Cell

M. Blatter[1], M. Sugnaux[1], C. Comninellis[2], K. Nealson[3], F. Fischer[1]*

[1]HES-SO Valais, [2]EPF Lausanne, [3]University of Southern California

Caustic soda is a key compound in a multitude of industrial processes. It is used in both organic and inorganic chemical industries, paper manufacturing as well as wastewater treatment [1]. Nowadays, NaOH is produced by the well-known chlor-alkali electrolysis process [2]; an energy consuming method [3] that generates chlorine gas as a by-product whose use is more and more questioned from a sustainable economical perspective. The microbial fuel cell (MEC) provides a new and more sustainable alternative, which offers the opportunity to clean wastewater while producing hydrogen and other useful compounds [4]. The advantage of a MEC in comparison to a classic electrolysis cell is that it takes advantage of microorganisms present within the anodic chamber to lower the needed applied voltage in comparison to water electrolysis where 1.22V are needed. With microbes the overpotential is reduced by a magnitude down to 0.13V [5]. Today, no model relative to NaOH generation for MEC is described on the literature. The same observation is valid concerning the well-known chlorination process.

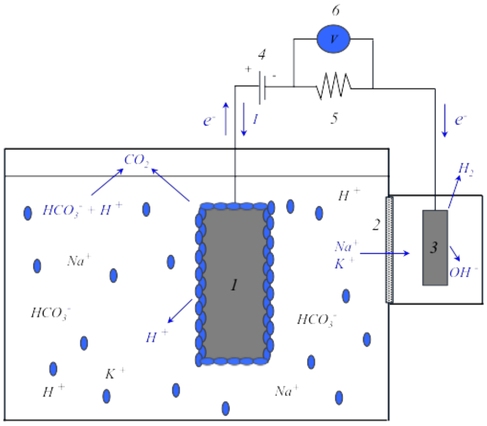


Figure 1. MEC for sustainable base generation and important parameters to establish a predictive model. (1) Anode covered by a biofilm composed of *Shewanella oneidensis* MR-1, (2) Nafion® membrane N-117 separating the two half cells, (3) platinum sputtered RVC cathode used for hydrogen generation, (4) external power supply, (5) 11Ω resistance, (6) multimeter.

The objective of the study was the creation of a predictive model for base generation. The latter allows anticipating the base generation by knowing the current generated by the system employed, its anolyte composition, the volume of catholyte utilized and the duration of the operation. The model established behaved in accordance to experimental conditions and can, therefore, be used in future as a predictive tool to estimate the base production of microbial/electrochemical processes.

[1] C. Kurt, J. Bittner, in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. 33, Wiley-VCH Verlag, Weinheim, **2003**, 371-382.
[2] P. Schmittinger, T. Florkiewicz, L.C. Curlin, B. Lüke, R. Scannell, T. Navin, E. Zelfel, R. Bartsch, in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. 8, Wiley-VCH Verlag , Weinheim, **2003**, 532-615.
[3] E.C. Committee, *An Electricity Intensive Sector Exposed to Carbon Leakage*, The European Chlor-Alkali industry, Brussels, **2010**.
[4] R.A. Rozendal, H.V. Hamelers, K. Rabaey, J. Keller, C.J. Buisman, *Trends Biotechnol.* **2008**, *26*, 450-459.
[5] H. Liu, H. Hu, J. Chignell, Y. Fan, *Biofuels* **2010**, *1*, 129–142.

Heterogeneous Catalytic Reactor for H_2 Production from Formic Acid for Use in PEM Fuel Cells

I. Yuranov[1], A. F. Dalebrook[1], G. Laurenczy[1]*

[1]EPF Lausanne

Hydrogen is considered as a carrier in energy production and storage systems due to its high gravimetric energy content and being H_2O the only product released when it is oxidized. Today, H_2 storage and transportation rely mostly on compressed and liquefied hydrogen, having safety and weight issues [1]. Formic acid (FA) is an alternative H_2 source [2]: catalytic dehydrogenation of FA yields only H_2 and CO_2 that can be used directly in appropriate PEMfuel cells. Since FA-based hydrogen generators will certainly find applications in future installations for power generation, we have developed a solid catalyst based reactor for on-demand H_2 generation from FA. The idea was to apply a heterogeneous catalyst allowing use of diluted FA (from biomass/bio-waste conversion) since it can be easily recovered/recycled.The catalyst was synthesized via immobilization of a homogeneous Ru(II)-tppts catalyst [3] on PPh_2-modified polystyrene (PS) beads (Fig. 1). FA decomposition was tested in a specially designed reactor (Fig. 2) in both semi-batch and continuous modes. The dependences of hydrogen production and gas-phase composition on the reaction conditions and reactor geometry were established. CO traces were eliminated (when it was necessary) through end-of-pipe PROX. It was shown that the proposed approach is scalable and provides a H_2 productivity suitable for PEM fuel cell applications. The obtained results will be discussed in the poster presentation.

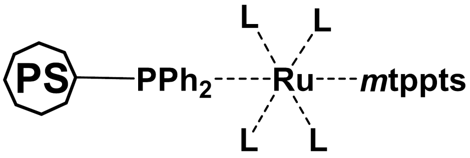


Figure 1. Immobilized catalyst structure.

Figure 2. Catalytic reactor and set-up.

Acknowledgements: We thank CTI, CCEM and EPFL for financial support. We are also grateful to Granit Technologies SA, PSI (Membranes Electrochemical Cells Group) and ICP ZHAW teams for the fruitful collaborations.

[1] A. Dalebrook, W. Gan, M. Grasemann, S. Moret, G. Laurenczy, *Chem. Comm.*, **2013,** *49*, 8735
[2] M. Grasemann, G. Laurenczy, *Energy Environ. Sci.,* **2012**, 5, 8171
[3] C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem. Int. Ed.,* **2008**, 47, 3966

Systematic Modeling and Validation of Long-term Waste Incineration Planning in Integrated Chemical Sites

T. P. Rodríguez Hernández[1], V. M. Bolis[1], M. L. Abächerli[1], E. Capón-García[1], K. Hungerbühler[1]

[1]ETH Zürich

Waste production is non-negligible in the process industry [1]. In the last decades, incineration has raised as a prominent method for industrial waste treatment. Its main benefits are: i) the significant reduction of waste volume; ii) the destruction of toxic and hazardous substances; iii) the possibility of on-site treatment, thus allowing for lower transport distances and risk reduction; and iv) the possibility to partially recover the energy contained in the waste [2]. Thermal waste valorization is an important feature in industry towards higher energy efficiency. This is especially interesting considering that the Swiss chemical industry is responsible for approximately 3.5 % of the gross energy consumption, of which 55% stems from fossil fuels and 23% from nuclear [3].

Previous studies have shown that the systematic scheduling of waste incineration in integrated chemical sites can lead to both economic and environmental benefits in the short and medium term. This work aims to optimize long-term planning decisions of waste management in an incineration site. The approach is validated based on historical waste production data obtained from a chemical site in Wallis.

The optimization problem is formulated as a mixed-integer linear model (MILP) with a discrete time representation. The planning horizon length is 5 years, subdivided in periods of one week. The underlying system comprises waste production facilities, different means of waste transfer, as well as waste storage and incineration units. Mass and energy balances of the various units are included in the model, together with economic aspects, regulations and process restrictions, such as emission limits and storage capacities. The objective is to maximize the amount of waste treated on site. Based on a given waste production forecast and the imposed objective, the model provides an optimal long-term plan for treating, transferring and storing waste on site. Furthermore, the model also provides the incineration performance, including air, natural gas and water consumption as well as carbon dioxide emissions, and how storage and treatment capacities could be expanded.

In the considered integrated chemical site, waste is produced in different in-house facilities and stored nearby. From there, waste is transferred by tank trucks, tank wagons or through pipelines to intermediate storage tanks by the incineration plant or directly to one of the two incineration units for direct combustion. Different kinds of waste can be treated simultaneously in the same incineration unit, as long as they belong to the same treatment campaign. In this specific case, waste streams are assigned to one of five different treatment campaigns.

The model outcome, based on historical data from 2010 to 2014, is compared to the real process performance measured by the industrial partner in the same period, in order to validate the model and assess the improvement potential of the site. Results prove the applicability of the introduced optimization model to industrial routines and thus legitimize its extrapolation, adaptation and usage to optimize waste management in other treatment sites for upcoming planning periods based on waste forecasts. In a further step, the developed model can be applied to integrate multi-objective frameworks in the optimization of networks consisting of multiple incineration sites, thus considering a national perspective to assess the contribution of industrial waste incineration to the energy turnaround.

[1] Poliakoff, M., Fitzpatrick, J.M., Farren, T.R., Anastas, P.T., 2002. Green Chemistry: Science and Politics of Change. Science 297, 807-810
[2] Williams, P.T., 2005. Waste treatment and disposal, 2nd ed. Wiley.
[3] Swiss Federal Office for the Environment (FOEN), 2015, Entsorgung von Sonderabfällen von 2003 bis 2014

Sub-nanometre gold particles catalyse transfer hydrogenation of N-heterocyclic compounds

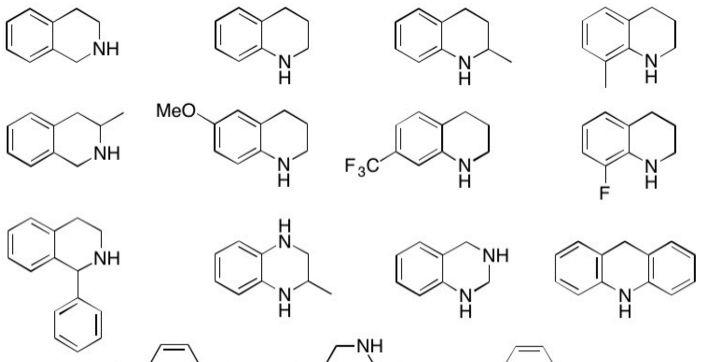
B. Vilhanová[1,2], M. Ranocchiari[1], J. A. van Bokhoven[1,2]*

[1]Paul Scherrer Institute, [2]ETH Zurich

Saturated N-heterocyclic compounds are highly desired building blocks in the pharmaceutical industry as they represent the core of numerous active pharmaceutical ingredients. Such compounds can be prepared by hydrogenation of the corresponding unsaturated analogues, such as derivatives of quinoline, isoquinoline, quinoxaline, acridine, etc.

Our group recently reported the synthesis of exceptionally small (0.8 ± 0.2 nm) gold particles supported on 3-aminopropyl-functionalized silicate SBA-15, which were highly active and selective in the dehydrogenation of formic acid.[1] Assuming that the sub-nanometre gold particles can have a bigger potential for applications in catalysis, we continued our research in this direction. As a result, we report here the application of our material in transfer hydrogenation of various N-heterocyclic compounds with a high selectivity, activity, and large substrate scope.

The figure below shows the products obtained in more than 90% isolated yield and high purity by transfer hydrogenation using the catalyst (1 mol% of gold) with $HCOOH/Et_3N$ in anhydrous DMF. The catalyst could be recycled 5 times without loss in catalytic activity.



[1] Beloqui Redondo, A.; Ranocchiari, M.; van Bokhoven, J. A. Synthesis of sub-nanometer gold particles on modified silica. *Dalton Trans.* **2016**, *45*, 2983–2988.

A novel strategy of activating hematite photoanodes for solar water oxidation

C. Cui[1]

[1]University of Zurich

Hematite has emerged as a promising photoanode for solar water oxidation owing to its abundance, non-toxicity, chemical stability, favorable band gap of 2.0~2.2eV for broad visible light absorption, and suitable valence band edge position. However, the very poor electrical conductivity of intrinsic hematite limits both the electron transport to the current collector and the hole diffusion to the semiconductor/electrolyte interface. Yet the very high activation temperature 650-800 ^{o}C usually needed deforms the glass substrate and degrades the FTO layer.

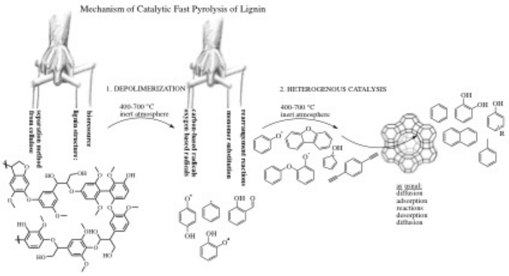
The goal of this study is the development of new materials processing and new structures for increasing the electrical conductivity and suppressing the recombination of photo-excited charge carriers within α-Fe_2O_3 as well as accelerating the catalytic reaction kinetics for water oxidation.

The Mechanism of Catalytic Fast Pyrolysis

V. Custodis[1,2], P. Hemberger[2], J. A. van Bokhoven[1,2]*

[1]ETH Zurich, [2]Paul Scherrer Institute, Villigen

Lignin is an abundant biopolymer as only resource for renewable phenols and aromatics but still regarded as a waste product from paper and pulp production. While cellulose and hemicellulose are regular biopolymers and thus easily converted,[1] lignin is highly disordered comprising differently substituted phenols connected by various bonds, such as carbon-carbon and ether bonds. The structure of lignin highly depends on separation method, bioresource and storage. This is why efficient conversion into useful chemicals is very hard. The process of catalytic fast pyrolysis of lignin is much more complicated than standard heterogeneous catalytic processes. Additionally to the constraints of diffusion, adsorption and desorption, primary depolymerization and diffusion out of the polymeric matrix of lignin is necessary.[2] The depolymerization is mainly driven radically and has to be considered when improving the process of CFP. We study the mechanism of primary depolymerization at high vacuum with iPEPICO at the Swiss Light Source.



Besides detection of all the primary radicals isomer-specifically we correlate those results with the observations at ambient pressure and with longer residence times as well as with the actual lignin depolymerization yields and selectivities. We investigated the influence of structural differences resulting from the separation method of lignin onto the catalytic fast pyrolysis products. Fast depolymerization is achieved by pyrolysis[3] and catalytic fast pyrolysis (CFP) to temperatures up to 650°C yields the largest amount of phenolic monomers.[4] The reactions of primary products are mainly determined by the nature of the formed radical: Substituents, such as methoxy-groups, enable stabilization and internal rearrangements of the radicals, while plain aromatics and phenols rather recombine immediately, to form dibenzofurane.[5] This observation is supported by the fact that lignins with a high content of multiple methoxy-substituted phenolic subunits produce more monomers at high temperature, thus less recombination occurs. The prominent bonds –main difference between carbon-carbon and ether bonds- require different active sites in the catalyst to convert effectively.[6] While carbon-carbon bonds are easily broken by H-USY, as known from FCC, ether bonds result in lower monomer yield and higher selectivity for phenols instead of aromatic hydrocarbon. Thus the lignin structure is crucial for the product distribution of CFP and must be optimized accordingly.

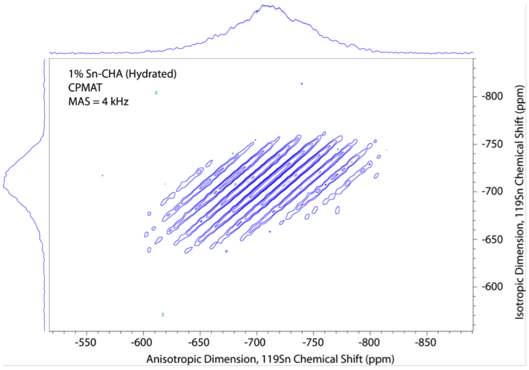
[1] G.W. Huber, S. Iborra, A. Corma, Chem. Rev., 106, pp. 4044–4098, 2006.
[2] M. Brebu, C. Vasile, Cellul. Chem. Technol., 44, pp. 353–363, 2010.
[3] Z. Ma, E. Troussard, J.A. van Bokhoven, Appl. Catal. A Gen., 423-424, pp. 130–136 2 012.
[4] D. Mohan, C.U. Pittman,, P.H. Steele, Energy Fuels., 20, pp. 848–889, 2006.
[5] V.B.F. Custodis, P. Hemberger, Z. Ma, J.A. van Bokhoven, J. Phys. Chem. B., 118, pp. 8524–8531, 2014.
[6] V.B.F. Custodis, C. Bährle, F. Vogel, J.A. van Bokhoven, J. Anal. Appl. Pyrolysis., 115, pp. 214–223, 2015.

Structural Characterization of Sn Sites in Sn-Chabazite by Dynamic Nuclear Polarization Enhanced Solid-State NMR

T. Ong[1], W.-C. Liao[1], A. Comas-Vives[1], J. W. Harris[2], R. Gounder[2], C. Copéret[1]

[1]ETH Zurich, [2]Purdue University

Chabazite (CHA) is a small-pore (3.8 Å diameter windows), highly symmetric zeolite with only one symmetry-unique T site, in contrast with the more structurally complex Beta zeolite that has nine unique T sites. The uniformity of CHA T sites suggests that it should be relatively straightforward to establish the zeolite’s structure-activity relationship, and may help in our understanding of more complex zeolites. In this work, we use dynamic nuclear polarization (DNP) enhanced solid-state NMR to examine the Sn sites in 1 wt % Sn-CHA zeolites. The number of Lewis acidic Sn sites located within the framework, and only those sites located at external crystallite surfaces, are quantified respectively by titration with CD_3CN and pyridine and infrared spectroscopy. We use cross polarization magic angle turning (CPMAT) to obtain the chemical shift anisotropy (CSA) parameters of ^{119}Sn in the zeolite framework (spectrum shown in Figure), which in combination with Density Functional Theory (DFT) calculations allows elucidation of the chemical nature of the Sn site. The effects of dehydroxylation, as well as binding of small molecules such as water and pyridine, on the resulting ^{119}Sn solid-state NMR spectra are investigated.

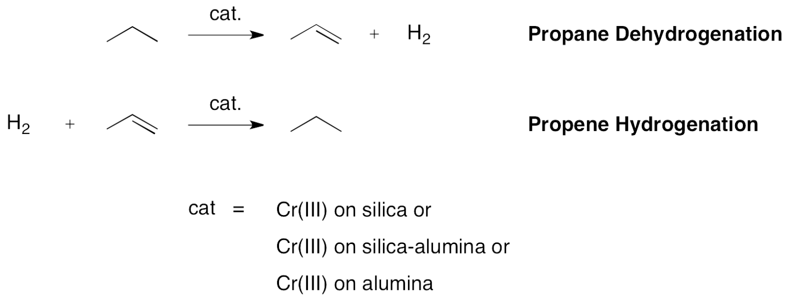


Mechanistic Insights for Propane Dehydrogenation and Propene Hydrogenation on Cr(III) Aluminates and Cr(III) Silicates

M. F. Delley[1], D. P. Estes[1], K. V. Kovtunov[2], I. V. Koptyug[2], C. Copéret[1]*

[1]ETH Zurich, Switzerland, [2]International Tomography Center, Novosibirsk, Russia

Ethylene polymerization and propane dehydrogenation are industrially performed using chromium on oxide supports (CrO_x/SiO_2 or CrO_x/Al_2O_3).[1] Despite more than 50 years of extensive research, the nature of the active sites and the mechanism is still a matter of controversy for both processes. A molecular level understanding is made difficult by the complicated nature of the heterogeneous catalysts, the presence of multiple Cr sites and a low amount of active species.



We have previously demonstrated that well-defined Cr(III) on silica prepared via a molecular approach and characterized by a combination of spectroscopic techniques (IR, EPR, XAS, UV/Vis, adsorption of probe molecules) are active in both ethylene polymerization and propane dehydrogenation.[2] Using a similar approach we recently obtained well-defined Cr(III) on silica-alumina and Cr(III) on alumina and investigated propane dehydrogenation and the reverse reaction, propene hydrogenation. Here, we discuss the effect of the support and mechanistic insights into hydrogenation using a combination of kinetic investigations and Parahydrogen Induced Polarization (PHIP) experiments.

[1] a) McDaniel, M. P. *Adv. Catal.* **2010**, *53*, 123. b) Sattler, J. J. H. B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B. M. *Chem. Rev.* **2014**, *114*, 10613.
[2] a) Delley, M. F.; Nunez-Zarur, F.; Conley, M. P.; Comas-Vives, A.; Siddiqi, G.; Norsic, S.; Monteil, V.; Safonova, O. V.; Coperet, C. *PNAS* **2014**, *111*, 11624. b) Conley, M. P.; Delley, M. F.; Nunez-Zarur, F.; Comas-Vives, A.; Coperet, C. *Inorg. Chem.* **2015**, *54*, 5065. c) Delley, M. F. *CHIMIA* **2015**, *69*, 168.

Dry-reforming of methane over bimetallic Ni-M/La_2O_3 (M = Co, Fe): The effect of the rate of $La_2O_2CO_3$ formation and phase stability on the catalytic activity and stability.

A. Tsoukalou[1], Q. Imtiaz[1], S. Kim[1], P. M. Abdala[1], S. Yoon[2], C. Müller[1]*

[1]ETH Zurich, [2]EMPA

The dry reforming of methane (DRM) converts two major greenhouse gases into a valuable synthesis gas with a H_2:CO ratio close to 1, *i.e.* a ratio that is favourable for the production of liquid hydrocarbons *via* Fischer-Tropsch synthesis [1,2]. Ni is arguably the most attractive catalyst for the DRM since it combines a high DRM activity and comparatively low cost (when compared to precious metals). However, at the same time Ni is prone to sintering and coking. [3] Previous reports, albeit being partially contradictory, have indicated that the alloying of Ni with inexpensive transition metals, *e.g.* Co or Fe affects the activity and stability of Ni-based catalysts under dry reforming conditions. [4-11] In this work we critically assess the catalytic performance of Ni-based bi-metallic catalysts derived *via* the reduction of perovskite precursors, *i.e.* $LaNi_{0.8}M_{0.2}O_3$ (M = Co and Fe). After reduction, the perovskite structure collapsed and Ni, Ni-Fe or Ni-Co particles embedded in a La_2O_3 matrix were obtained. *In-situ* XRD and energy dispersive X-ray spectroscopy techniques were employed to probe metal-metal and metal-support interactions and phase transformations under reactive conditions. Ni-Co was found to be the most active catalyst, whereas Ni-Fe showed no activity. We observed that the addition of Co increases the rate of $La_2O_2CO_3$ formation, which in turn enhances the removal of carbonaceous deposits from neighbouring active sites, thus, leading to a catalyst with an increased stability and activity. The poor activity of Ni-Fe was explained by Fe and Ni de-alloying under reactive conditions and the encapsulation of the Ni particles by $LaFeO_3$.

[1] M.C.J. Bradford, M.A. Vannice, Catal Rev, 41, **1999**, 1-42.
[2] I. Wender, Fuel Process Technol, 48, **1996**, 189-297.
[3] D.L. Trimm, Catal Rev, 16, **1977**, 155-189.
[4] S.M. de Lima, J.M. Assaf, Catal Lett, 108, **2006**, 63-70.
[5] J. Estephane, S. Aouad, S. Hany, B. El Khoury, C. Gennequin, H. El Zakhem, J. El Nakat, A. Aboukais, E.A. Aad, Int J Hydrogen Energ, 40, **2015**, 9201-9208.
[6] J.G. Zhang, H. Wang, A.K. Dalai, J Catal, 249, **2007**, 300-310.
[7] D. San-Jose-Alonso, J. Juan-Juan, M.J. Illan-Gomez, M.C. Roman-Martinez, Appl Catal a-Gen, 371, **2009**, 54-59.
[8] G. Valderrama, A. Kiennemann, M.R. Goldwasser, Catal Today, 133, **2008**, 142-148.
[9] G.S. Gallego, C. Batiot-Dupeyrat, J. Barrault, E. Florez, F. Mondragon, Appl Catal a-Gen, 334, **2008**, 251-258.
[10] M. Koike, D. Li, Y. Nakagawa, K. Tomishige, ChemSusChem, 5, **2012**, 2312-2314.
[11] K. Sutthiumporn, T. Maneerung, Y. Kathiraser, S. Kawi, Int J Hydrogen Energ, 37, **2012**, 11195-11207.

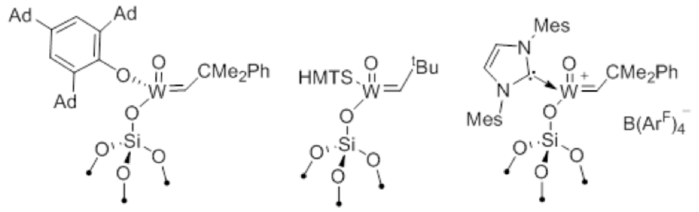
Cationic Silica-Supported N-Heterocyclic Carbene Tungsten Oxo Alkylidene Sites: Highly Active and Stable Catalysts for Olefin Metathesis

M. Pucino[1], V. Mougel[1], A. Fedorov[1], C. Copéret[1]*

[1]ETH Zurich

Despite significant advances in the last years, designing supported alkene metathesis catalysts with high activity and stability is still a challenge. Here, we present a generation of well-defined silica-supported cationic tungsten alkylidene complex which displays unprecedented performances in terms of activity and stability. Thissilica-supported N-heterocyclic carbene tungsten oxo alkylidene complex was designed in light of last results obtained showing that the increased σ donation ability of the ancillary ligand at the metal center results in a better activity for metathesis of terminal olefins and higher stability towards deactivation *via* ethylene poisoning[1].

1-nonene homometathesis test, 30°C



	1	**2**	**3**
mol%	0.1	0.02	0.02
TOF$_{3min}$ **(%of conversion)**	5 (2%)	37 (4%)	946 (6%)
time to equilibrium	42% of conversion after 24h	48h	5h

First, $[W(=O)(=CHCMe_2Ph)(IMes)(OtBuF_6)]$ $[B(ArF)_4]$[2] was grafted onto $SiO_{2\text{-}700}$ to afford the corresponding surface species, which was fully characterized by mass balance analysis and spectroscopic techniques (IR, NMR, ss-NMR). The activity of this material was then investigated towards self-metathesis, ring-closing metathesis and cross-metathesis with functionalized substrates in batch and flow conditions.The catalyst shows functional-group tolerance, unprecedented activity and exceptionally high stability for a broad range of substrates. For terminal olefins it was possible to reach extremely high turnover numbers: above 1.2 million for propene metathesis within 6 days and only 40% deactivation over that period[3]

This work highlights that a fine tuning of the structure and electronic properties of supported alkene metathesis catalysts allows for dramatic increase of activity and selectivity, thus showing the potential of such catalysts.

[1] A. Poater, X. Solans-Monfort, E. Clot, C. Copéret, O. Einstein, *J. Am. Chem. Soc.*, **2007**, 129, 8207-8216; V. Mougel, M. Pucino, C. Copéret, *Organometallics,* **2015**, 34, 551 – 554.
[2] R. Schowner, W. Frey, M. R. Buchmeiser, *J. Am. Chem. Soc.*, **2015**, 137, 6188 – 6191.
[3] M. Pucino, V. Mougel, R. Schowner, A. Fedorov, M. R. Buchmeiser, and C. Copéret*Angewandte Chemie - International Edition*, **2016**, 55, 4300-4302.

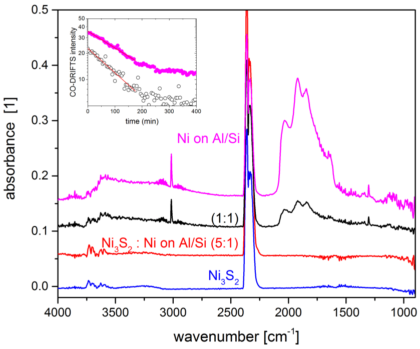
Sulfur on nickel catalysts impedes the desorption of reaction products

J. Terreni[1,2], D. Bleiner[1], A. Borgschulte[1,2]*

[1]Empa, [2]University Zürich

Metallic nickel is known as a perfect methanation catalyst [1]. However, omnipresent sulfur contaminants in the process gas lead to the chemisorption of sulfur on nickel and eventually to the formation of nickel sulfides. Compared to nickel, nickel sulfide displays a negligible catalytic activity. The nickel catalyst is thus deactivated (poisoned). Although this phenomenon is very well known [2], detailed knowledge on which of the various elementary steps of the methanation reaction is hindered by sulfur poisoning is lacking. For this, we study the catalytic activity of physically mixed samples of nickel on alumina/silica and nickel sulfide as a function of temperature and time. To obtain an insight into the atomistic mechanism, we utilized *operando* diffusive reflectance infrared Fourier transform spectroscopy (DRIFTS).

As expected, the results clearly show that the catalytic activity of the catalyst decreases with the amount of the sulfide. However, low content of nickel sulfide decreases the initial activity only to a lesser amount, but accelerates the decay of the long term activity. Together with spectroscopic data, we conclude that (i) sulfur is mobile on metallic nickel and (ii) sulfur changes the reaction path which (iii) accelerates the coverage of the active catalysts by (hydr-)oxides and carbonate species and leads eventually to a deactivation of the catalyst. This indicates that the established model of sulfur poisoning by a blocking of all catalytically active sites is too simple [3]. The results indicate a way to create a sulfur resistant methanation catalyst.



The figure shows DRIFTS spectra of physically mixed samples of nickel on alumina/silica and nickel sulfide in CO_2/H_2 at 300°C. The inset displays the time dependence of the intensity of the CO adsorbed to Ni.

[1] Manuel Götz, et al., *Renewable Energy*, **2016**, 85, 1371-1390
[2] Rudolf P.W.J. Struis, et al., *Applied Catalysis A: General,* **2009,** 362, 121–12
[3] E. L. Hardegree, Pin Ho, and J. M. White, *Surface Science.*, **1986**, 165, 488-506

Reaction intermediates and pathways for CO_2 hydrogenation on Cu/ZrO_2 catalysts: a combined DFT and experimental approach

K. Larmier[1], S. Tada[1], A. Comas-Vives[1], W.-C. Liao[1], C. Copéret[1]*

[1]ETH Zurich

CO_2 hydrogenation to methanol has become in the last decades a key reaction in CO_2 conversion processes toward fuels, plastics or chemicals.[1] Copper-based catalysts have been widely shown to be very active, although promoters[2] or support effects are required.[3] In particular, ZrO_2 was shown to be very interesting as a support for Cu particles.[3] Despite numerous studies dedicated to this reaction, the detailed reaction mechanism is still highly debated. Two main mechanisms have been proposed: the formate route or the reverse water-gas shift/CO hydrogenation route.[4,5] Herein, we use a combined experimental and theoretical study to investigate the mechanism for the hydrogenation of CO_2 on Cu/ZrO_2 catalysts.

We performed a stepwise hydrogenation of $^{13}CO_2$ using either H_2 or D_2 as a reactant, under different pressure conditions on a Cu/ZrO_2 sample. The catalyst was examined by solid-state NMR and IR spectroscopy after each step, in order to determine the existing surface species. The isotopic content of the produced methanol was identified by desorbing the surface species in H_2O or D_2O and recording liquid state NMR spectra. The results show that methanol can be formed by direct hydrogenation of formate. The latter can be formed under low pressures conditions, while its hydrogenation to methanol requires higher pressures.

DFT calculations (VASP, GGA level) were performed on a surface slab containing a copper nanoparticle (38 atoms) supported on a ZrO_2 slab. The most favourable computed pathway involves the activation of CO_2 at the metal support interface through the formate route. The results explain well the experimental results.

Finally, this pathway and the DFT-calculated rate constants were used to build a kinetic model that qualitatively reproduces well the experimental trends regarding the effect of the reaction pressure on the intermediates population.

[1] Goeppert et al., *Chem. Soc. Rev.*, **2014**, 43, 7995-8048
[2] Behrens et al., *Science*, **2012**, 336, 893-897
[3] Fischer et al., *J. Catal.*, **1997**, 172, 222-237
[4] Kim et al., *ACS Catalysis*, **2016**, 6, 1037-1044
[5] Yang et al., *ACS Catalysis*, **2015**, 5, 7328-7337

Synthesis of mordenite with targeted aluminum site distribution using structure directing agents

A. Knorpp[1], A. Pinar[2], M. Ranocchiari[2], J. A. van Bokhoven[1,2]*

[1]ETH Zurich, [2]Paul Scherrer Institut

The selective activation of methane is of high industrial and academic interest [1]. Copper exchanged zeolites such as Cu-mordenite and Cu-ZSM-5 are active in the stepwise conversion of methane to methanol. However, only a low fraction of the copper present participates actively in this conversion [2], and there is still much debate in the scientific community on the precise copper speciation responsible for catalytic activity.

What further complicates the elucidation of the copper species is the fact that location and speciation of the copper are influenced by the location and proximity of the aluminum sites in the zeolite framework. In zeolite synthesis, partial replacement of silicon by aluminum in the zeolite framework results in a local negative charge. This negative charge can be balanced by catalytically active species—the copper in this case—which provide a balance to this negative charge. Aluminum location itself is not fully understood, and it largely depends on the synthesis conditions. Therefore, the choice of synthesis conditions may provide an opportunity to control the aluminum distribution that contributes to the most active copper species.

We approach this topic with a holistic approach by starting with variation of synthesis conditions, and we seek to control the placement of aluminum. In particular we are studying the use of “structure directing agents” (SDAs) and the cooperation of multiple SDAs in the synthesis. This approach has been successful for controlling the aluminum placement in such zeolites as ferrierite [3]. Here we attempt to expand the use of cooperative SDAs to synthesize mordenite—a known methane-to-methanol catalyst—to selectively place aluminum and copper in its structure. The effect of synthesis conditions and resulting materials are characterized.

[1] R. Horn, R. Schlögl, *Cat. Let.,* 145 (2015) 23.
[2] M.H. Groothaert, P.J. Smeets, B.F. Sels, P.A. Jacobs, R.A. Schoonheydt, *J. Am. Chem. Soc*. (2005) 127, 1394.
[3] Pinar, A.B., Gomez-Hortiguela, L., Perez-Pariente, *J. Chem. Mater.* (2007) 19 5617-5656.

Methane Activation: Transformation to Ethylene, Aromatics and Other Species

P. Sot[1], C. Copéret[1], J. A. van Bokhoven[1,2]*

[1]ETH Zurich, [2]Paul Scherrer Institute, Villigen

The transformation of methane to ethylene, aromatic molecules and methanol is intensively researched due to increasing amount of methane available on a market and environmental issues related to its production or utilization. We explore the possibility of using iron-based materials for transformation of methane to ethylene and aromatics. For the synthesis of these catalysts, multiple methods have been used, including aqueous ion exchange on zeolitic materials (such as ZSM-5) and grafting of a molecular precursor onto surface of silica, their thermal treatment and formation of single iron sites. The molecular precursors used for grafting are based on Fe(II) siloxide and Fe(III) siloxide, following Tilley, T. D. et al. [1,2] and Bao, X. et al. [3] The obtained materials were characterized and tested for their ability to catalyze C-H bond activation of methane in flow and batch reactors.

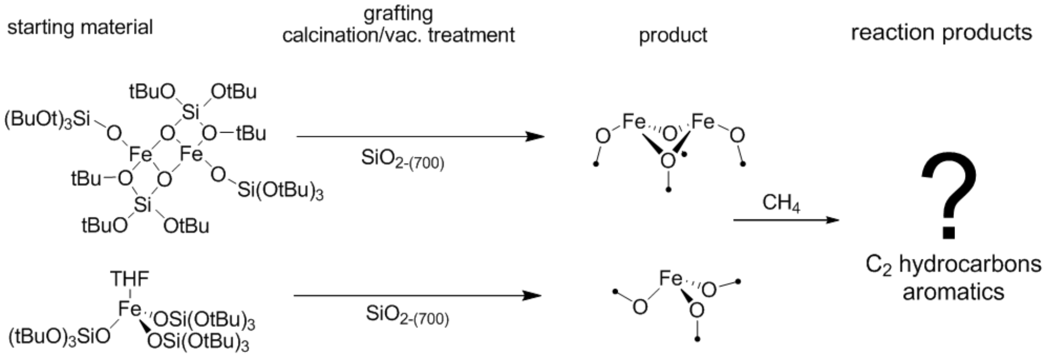


Figure 1. Grafting, thermal treatment and subsequent reaction with methane of iron(II) and iron(III) on silica.

[1] Tilley, T. D. et al. J. Catal (2005), 235 (1), 150-163
[2] Tilley, T. D. et al. J. Am. Chem. Soc. (2002), 124 (44), 13194-13203
[3] Bao, X. et al. Science(2014), 344 (6184),616-619

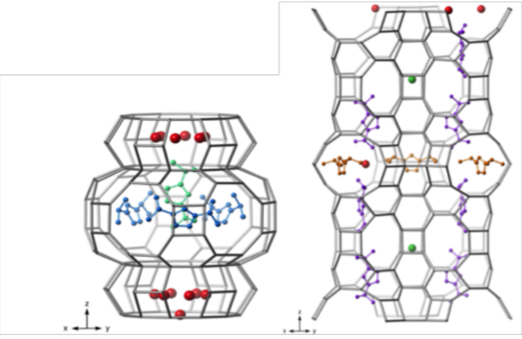
Structure analysis of Zn-DAF-1

A. Pinar[1], L. McCusker[2]

[1]Paul Scherrer Institut, [2]ETH Zurich, [3]Chevron ETC

A novel zincoaluminophosphate (Zn-DAF-1) with the **DFO**-type framework structure has been obtained using *N*,*N*'-di-isopropyl-imidazolium (DIPI) cations as the structure directing agent (SDA). In the past, this structure had only been synthesized as a Mg-AlPO (Mg-DAF-1) by the group of Paul Wright[1]. The **DFO** framework has two types of 12-ring channels: one with a uniform cross section (channel A) and the other with an undulating one (channel B), forming two types of large cavities. Attempts to locate the SDA species in Mg-DAF-1 using single-crystal diffraction data were not successful. This was attributed to the disorder of the organic species. For Zn-DAF-1, our structure analysis using synchrotron powder diffraction data allowed not only the positions of the Zn atoms in the framework, but also those of the DIPI cations and some fluoride ions and water molecules to be located in the pores[2].

The first DIPI cation, DIPI-1, is close to the walls of the large cavity in channel B and DIPI-2 lies approximately perpendicular to it at the center of the cavity (Fig. 1), forming a "super SDA" that, to the best of our knowledge, has not been observed before. All four DIPI positions seem to play a structure-directing role rather than just filling the void space of the structure, and this is probably the reason their positions could be determined.



[1] P. A. Wright, R. H. Jones, S. Natarajan, R. G. Bell, J. Chen, M. B. Hursthouse and J. M. Thomas, *Chem. Commun.*, **1993**, 633.
[2] A. B. Pinar, L. B. McCusker, C. Baerlocher, S.-J. Hwang, D. Xie, A. Benin, S. I. Zones, New J. Chem., 2016, DOI: 10.1039/C5NJ02897C.

Effect of noble metal nanoparticles on the conduction band electrons in UV-excited titania nanocrystallites for photocatalytic applications

A. Schneider[1], J. A. van Bokhoven[1]*

[1]ETH Zurich/PSI Villigen

Titania (TiO2) in both its rutile and anatase crystalline phases is a semiconductor which has been used for many photocatalytic applications. The presence of additional noble metal nanoparticles often enhances the conversion rates since they act as co-catalysts. However, the metal also impacts the behaviour of the energetic electrons that drive the catalytic reactions.

We have studied the high-frequency photoconductivity in titania nanocrystallites using UV pump/terahertz probe spectroscopy. This technique is based on the fact that short broadband pulses of electromagnetic radiation (terahertz pulses) are partially absorbed in a conducting sample; the change in the terahertz transmission after illumination with a UV laser pulse (wavelength 350 nm) therefore allows to characterize the photoexcited conduction band electrons.

We found that both gold and palladium nanoparticles lead to a dramatic increase of the number of free electrons in titania, even at a weight fraction as small as 0.3% (see figure 1); the effects of both metals are very similar. A surprising observation is the frequency dependence of the photoconductivity which drops to small values at low frequencies. This cannot be explained by the frequently used Drude model, but it rather demonstrates that the electrons are effectively confined within the titania nanocrystallites. One can conclude that for catalytic applications, it is preferential to have these crystallites in the form of free floating nanoparticles rather than in larger clusters, where a majority of the free electrons will not get to the interface of the catalyst with the solvent where the chemical reactions take place.

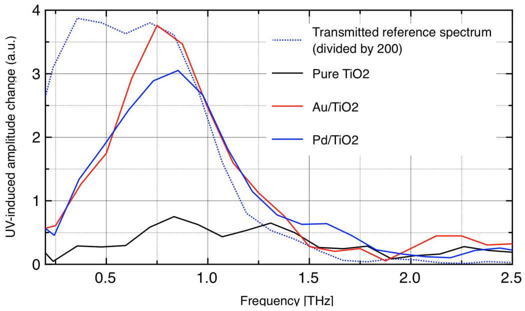


Figure 1: UV-induced transient terahertz absorption in three different titania samples. Compared to pure titania, the presence of noble metal nanoparticles leads to a 4 to 5-fold increase in the number of conduction band electrons.

Computational investigation and design of biomimetic cubane water oxidation catalysts

S. Luber[1], F. Hodel[1]

[1]University of Zurich

Solar energy is an inexhaustible energy source for a sustainable solution to the global energy consumption. The storage of large amounts of light energy can be achieved by conversion into chemical energy saved in biomass. Artificial photosynthesis permits the splitting of water into molecular hydrogen and oxygen and is therefore a very promising strategy to meet the increasing worldwide need for clean energy. This requires the development of high-performance water-reduction and water-oxidation catalysts (WOCs) where the latter is currently the main bottleneck for efficient photocatalytic water splitting. Very recently, the first Co(II)-based cubane WOCs (JACS, 2013, 135, 18734 (highlighted in Chimia issue 3-2014); JACS, 2015, 137, 11076 (highlighted in Chimia issue 11-2015)) have been presented, which excel through unprecedented structural analogies to the oxygen-evolving complex of nature's photosystem II. We study their properties and catalytic behavior by means of density functional theory (DFT) in combination with DFT-based molecular dynamics (ACS Cat. 2016, 6, 1505; submitted), which paves the way for smart design of bio-inspired high-performance WOCs.

Catalyst and process design for glycerol valorization to commodities

G. M. Lari[1], C. Mondelli[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich

Recently, many research efforts have been directed toward the valorization of the burgeoning amounts of glycerol obtained as a byproduct in the production of biodiesel. Lactic acid has been often targeted in view of its numerous applications and the limited productivity and scalability of its current manufacture by sugar fermentation. After demonstrating its advantageous manufacture from glycerol through the enzymatic oxidation to dihydroxyacetone and subsequent chemocatalytic isomerization,[1] we show the design of technical MFI zeolites containing small iron clusters as more efficient catalysts for the preparation of the ketonic intermediate.[2] We then unravel the intricate network of deactivation mechanisms affecting Lewis-acid tin-containing zeolites in the continuous liquid-phase conversion of dihydroxyacetone into lactic acid, finding that the alternative use of pyruvaldehyde as substrate would enable milder conditions, and thus improve their stability.[3] Identifying silver nanoparticles supported on acidic alumina as effective catalyst for the oxidehydration of glycerol to this aldehyde, we propose an improved process to manufacture lactic acid. Finally, we introduce hierarchical NaY zeolites comprising basic sites as more durable catalysts for the dehydration of lactic acid to acrylic acid compared to the state-of-the-art systems.[4] The industrial viability of these chemocatalytic processes (Fig. 1) is emphasized by process modelling and assessment studies, which evidence their environmental and economic benefits with respect to existing biocatalytic technologies.

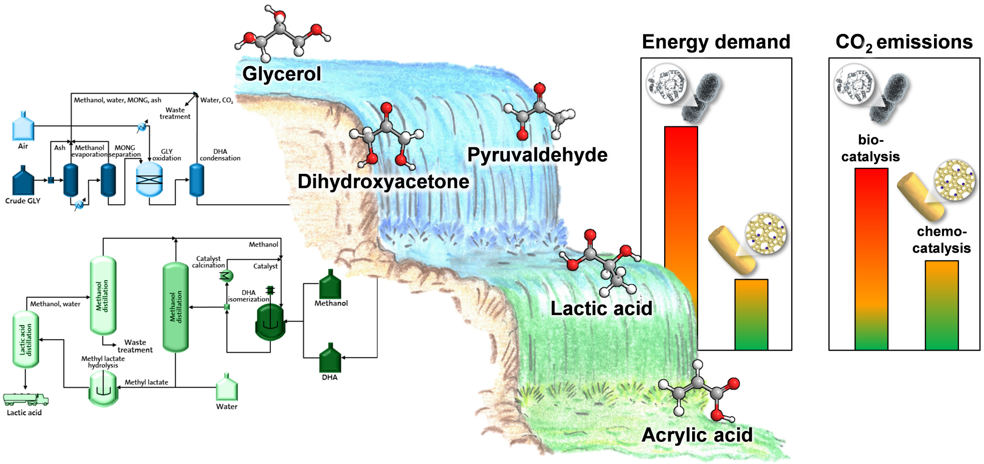


Figure 1 Chemocatalytic processes for glycerol valorization into lactic acid and derivatives.

1. M. Morales, P.Y. Dapsens, I. Giovinazzo, J. Witte, C. Mondelli, S. Papadokonstantakis, K. Hungerbühler, J. Pérez-Ramírez, *Energy Environ. Sci.* **2015**, 8, 558.
2. (a) G. M. Lari, C. Mondelli, J. Pérez-Ramírez, *ACS Catal.* **2015**, 5, 1453; (b) G.M. Lari, C. Mondelli, S. Papadokonstantakis, M. Morales, K. Hungerbühler, J. Pérez-Ramírez, *React. Chem. Eng.* **2016**, 1, 106.
3. G. M. Lari, P. Y. Dapsens, D. Scholz, S. Mitchell, C. Mondelli, J. Pérez-Ramírez,*Green Chem.* **2016**, 18, 1249.
4. G. M. Lari, B. Puértolas, M. S. Frei, Cecilia Mondelli, J. Pérez-Ramírez, *ChemCatChem* **2016**, 8, 1507.

Improved numerical methods for the characterization of zeolite catalysts by positron annihilation spectroscopy

A. Zubiaga[1], R. Warringham[1], S. Mitchell[1], P. Crivelli[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich

Positrons can be efficiently implanted into solids and interact with electrons in the structure in different ways. The formation of *ortho*-positronium (Ps), a long living electron-positron pair which exhibits a strong tendency to localize in open pore volumes and an annihilation rate proportional to the pore size, provides a unique opportunity to probe the pore connectivity within porous catalysts.[1] The availability of appropriate models is essential in order to relate the results of positron annihilation spectroscopy with the material properties. Due to the challenges in describing the behavior of Ps in solids by first-principles,[2] simplified single-particle models based on the Tao-Eldrup equation have become widely established to correlate the observed lifetime of Ps with the pore size. This model considers a single Ps particle in a well of spherical or rectangular geometry. However, it is highly limited when considering complex pore networks (*e.g.*, with different topology, degree of connectivity, and dimensionality) of similar size, such as those encountered in zeolite catalysts, which can lead to large discrepancies between the calculated lifetimes and experimental observations. To improve the description of Ps diffusion and annihilation in zeolites, here we develop an adaption of the Tao-Eldrup model that accounts for the specific crystallographic structure. This enables the assessment of the Ps localization, lifetime, and band structure, providing new insight into the existence and population of excited states and the transport mechanisms of Ps within zeolites of different framework types (Fig. 1). The model is validated by comparison with the lifetime values measured for well-crystallized zeolites attaining a good agreement in the trends. This versatile approach can be readily modified to address the impact of different guest species, including Brønsted acid centers, and crystal size.[3]

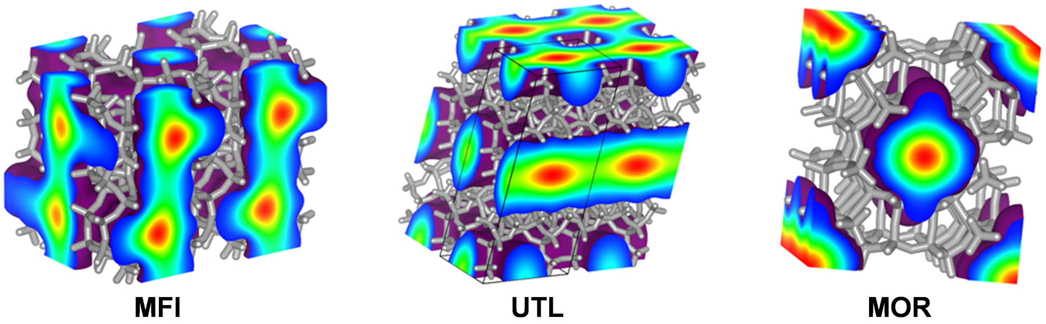


Figure 1 Calculated localization of Ps in zeolites with three-, two-, or one-dimensional frameworks.

1. A. Zubiaga, R. Warringham, M. Boltz, D. Cooke, P. Crivelli, D. Gidley, J. Pérez-Ramírez, S. Mitchell, *Phys. Chem. Chem. Phys.* **2016**, 18, 9211.
2. (a) M. Milina, S. Mitchell, D. Cooke, P. Crivelli, J. Pérez-Ramírez, *Angew. Chem., Int.* **2015**, 54, 1591; (b) M. Milina, S. Mitchell, P. Crivelli, D. Cooke, J. Pérez-Ramírez, *Nat. Commun.* **2014**, 5, 3922.
3. A. Zubiaga, M. M. Ervasti, I. Makkonen, A. Harju, F. Tuomisto, M. J. Puska, *J. Phys. B: At., Mol. Opt. Phys.* **2016**, 49, 064005.

Catalyst and process design for the preparation of sugar alcohols by epimerization-hydrogenation

G. Lari[1], O. Gröninger[1], C. Mondelli[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich

Sugar alcohols are commonly obtained by reduction of the corresponding saccharide and find multiple applications in the food, pharmaceutical, polymer, and fuel industries. In view of the rarity of some sugar substrates, epimerization of readily available monosaccharides has been proposed as a solution but a efficient catalytic systems are lacking.[1] Herein, we develop a molybdenum heteropolyacid-based catalyst to transform glucose, arabinose, and xylose into the less abundant mannose, ribose, and lyxose. We demonstrate that adsorption of molybdic acid onto activated carbon in its cesium form (Cs-HPA/C) limits leaching phenomena, leading to a greatly improved stability over 24 h on stream as compared to the protonic counterpart (H-HPA/C, Fig. 1a). Thereafter, we study the hydrogenation of the mixtures of epimers over ruthenium supported on carbon (Ru/C).[2] Advantageously, the precursor to the desired polyol is observed to reduce with a faster kinetics. This is being unraveled by density functional theory calculations. Finally, we assess different designs for a continuous chemocatalytic process for the conversion of glucose into mannitol. We find that the application of two reactors in series, the first dedicated solely to epimerization and the second containing a mixture of the epimerization and hydrogenation catalysts, allows the mannitol/sorbitol ratio to be increased from 1 to 1.5 with respect to the use of a single mixed-bed reactor (Fig. 1b). This opens the door for a prospective more efficient valorization of renewables to added-value chemicals.

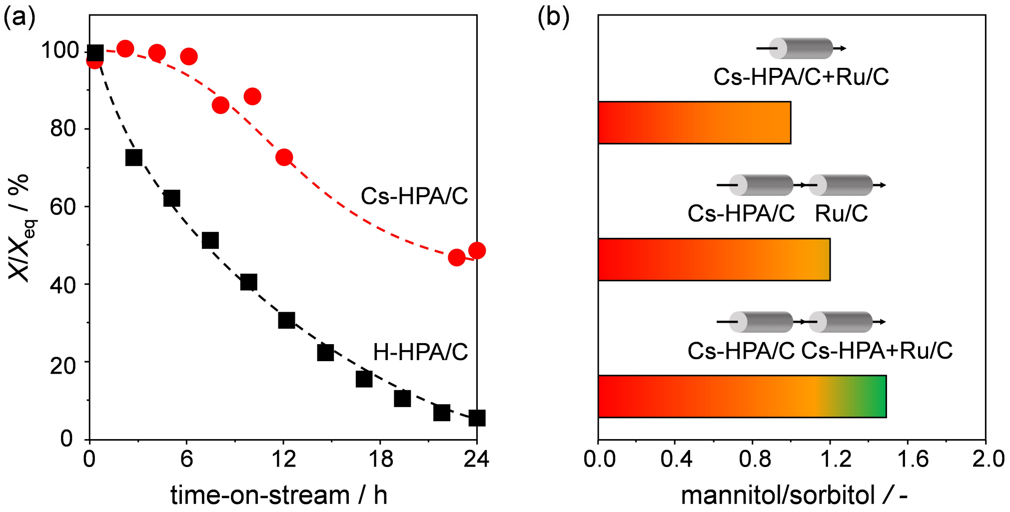


Figure 1 (a) Extent of epimerization over Cs- and H-HPA/C *vs*. time-on-stream and (b) mannitol/sorbitol ratio upon glucose conversion in different reactor configurations: (i) mixed bed, (ii) sequential Cs-HPA/C and Ru/C beds, and (iii) sequential Cs-HPA/C and mixed beds.

1. F. Ju, D. Van der Velde, E. Nikolla, *ACS Catal*. **2014**, 4, 1358.
2. J. V. Karabinos, A. T. Ballun, *J. Am. Chem. Soc*. **1953**, 75, 4501.

Enhanced electrocatalytic reduction of CO_2 to CO over Cu-based composites: catalyst equilibration is the key

G. O. Larrazábal[1], A. J. Martín-Fernández[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich

Combining the electrochemical reduction of CO_2 (eCO_2RR) with renewable energy sources is an attractive approach for recycling carbon emissions.[1] In particular, reducing CO_2 to CO would yield a versatile compound for the production of liquid fuels and plastics. The practical application of this reaction still demands the development of more active and stable electrocatalysts, which are selective to CO over other reduction products and inhibit the competing hydrogen evolution reaction (HER) in aqueous media.[2] Cu-In catalysts have recently emerged as promising candidates, although the structural basis behind the synergistic behavior of these metals remained unclear.[3] In this context, we have found that Cu-In nanoalloys are generated *in situ* under eCO_2RR conditions and that their structure evolves in parallel with an increase in the activity and selectivity for CO evolution over successive electrolytic cycles. Specifically, Cu-rich cores surrounded by $In(OH)_3$ shells are formed upon this equilibration stage (Fig. 1). Remarkably, the presence of $In(OH)_3$ plays a key role in maintaining a high selectivity for CO, in line with previous findings on Ag-In catalysts.[4] Based on this insight, we report the further development of multicomponent Cu-based catalysts with nanoengineered architectures aimed at exploiting such synergistic effects for the reduction of CO_2 to CO.

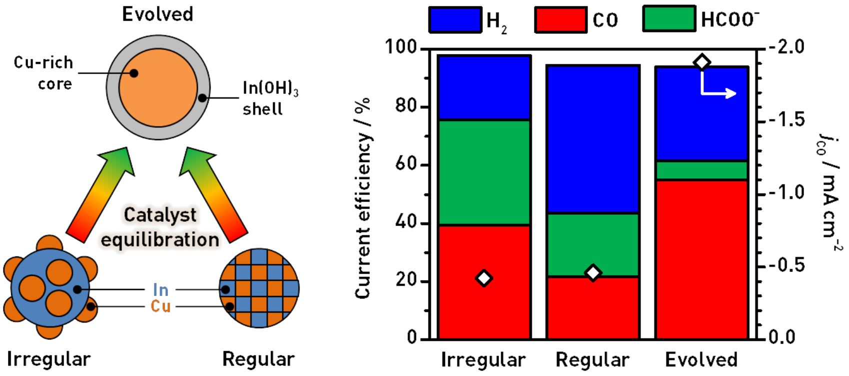


Figure 1 Cu-In nanoalloy catalysts converge after an equilibration phase towards a common core-shell-like structure with high activity and selectivity for the reduction of CO (performance shown at −0.6 V *vs.* RHE in CO_2-saturated 0.1 M $KHCO_3$).

1. E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazábal, J. Pérez-Ramírez, *Energy Environ. Sci.* **2013**, 6, 3112.
2. A. J. Martín, G. O. Larrazábal, J. Pérez-Ramírez, *Green Chem.* **2015**, 17, 5114.
3. A. Jedidi, S. Rasul, D. Masih, L. Cavallo, K. Takanabe, *J. Mater. Chem. A* **2015**, 3, 19085.
4. G. O. Larrazábal, A. J. Martín, S. Mitchell, R. Hauert, J. Pérez-Ramírez, *J. Catal.* **2016**, doi:10.1016/j.jcat.2015.12.014.

Sustainable polyurethane raw materials through heterogeneous aluminosilicate catalysts: From active site quality to reactor design

T. Keller[1], M. O. Haus[1], J. Arras[2], J. Pérez-Ramírez[1]*

[1]ETH Zurich, [2]Covestro AG

Methylenedianiline (MDA) is the key intermediate for the most common isocyanate precursor of polyurethanes (*ca.* 15 Mt a^{-1}). Industrially, it is synthesized from the condensate of aniline and formaldehyde via a series of HCl-catalyzed rearrangements (Fig. 1a), resulting in a complex product mixture, whose composition in terms of MDA isomers, oligomers, and side-products decisively impacts the properties of the derived polyurethanes. For separation, the homogeneous catalyst has to be quenched with aqueous NaOH. This prevents its reutilization, and furthermore imposes an exhaustive wastewater treatment of the chloroamine-contamined brine. Accordingly, a heterogeneous replacement is heavily sought after, but there is often a large discrepancy between the conditions (*e.g.*, aniline:formaldehyde ratio, temperature profiles) employed in literature and in industry, making the assessment of the implementation potential difficult.

In this contribution, we report the development of aluminosilicate-based solid acid catalysts for MDA synthesis. Whereas amorphous silica-aluminas (ASAs) all yield similar MDA isomer distributions, zeolites evidence shape-selective properties that are determined by their crystal structure. These were found to be optimal for FAU-type zeolites, such as Y and USY. If the diffusion through the microporous domains is facilitated by an auxiliary mesopore network, they provide excellent activity, which can be quantified based on the product of their external surface area and their Brønsted acidity (Fig. 1b). However, although the enhanced diffusivity also retards their deactivation, the susceptibility of micropores to blockage by oligomers cannot be avoided. Accordingly, to find more stable catalysts, an in-depth study on non-microporous aluminosilicates was carried out to rationalize the impact of the preparation method on their composition, porosity, acidity, and ultimately on their catalytic performance. Through a kinetic model of an MDA reactor, we demonstrate how the advantages of zeolites (excellent selectivity) can be combined with the merits of ASAs (excellent stability) in a co-catalytic process, which would be an attractive option for the heterogeneously-catalyzed manufacture of MDA.

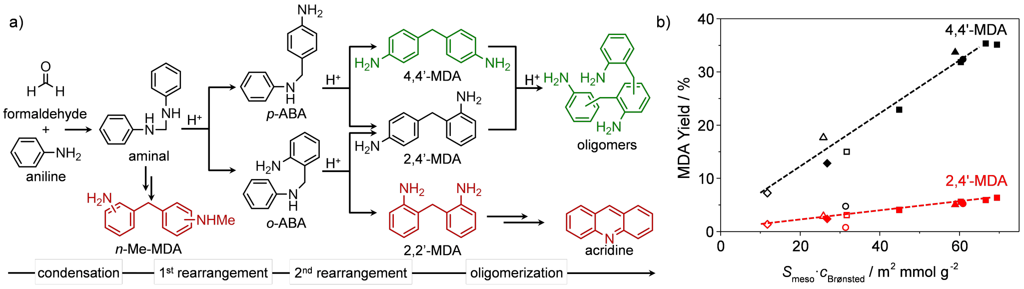


Figure 1. a) Reaction network for the synthesis of MDA. b) Linear correlation between the MDA yield and the product of external surface area and Brønsted acidity observed over conventional and hierarchical USY zeolites of varying composition and mesoporosity.

1. T. C. Keller, J. Arras, S. Wershofen, J. Pérez-Ramírez, *ACS Catal.* **2015**, 5, 734.

Stabilization of catalytically-active metal atoms on graphitic carbon nitride

E. Vorobyeva[1], Z. Chem[1], P. Midgley[2], R. Leary[2], J. Meurig Thomas[2], N. López[3], G. Vilé[1], S. Mitchell[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich, [2]University of Cambridge, [3]ICIQ

Single-atom heterogeneous catalysts (SAHCs) receive considerable attention aiming to combine the excellent metal utilization attained by homogeneous catalysts with the robustness and facile recovery offered by traditional heterogeneous catalysts. Thanks to the so-called ‘six-fold cavities’ and the rich nitrogen content in the structure, mesoporous graphitic carbon nitride (mpg-C_3N_4) appears to be an attractive support for anchoring and stabilizing metal atoms. Very recently, a SAHC based on Pd on mpg-C_3N_4 was shown to efficiently convert 1-hexyne into 1-hexene with greater than 90% selectivity (Fig. 1).[1] The atomic dispersion of the metal throughout the sample was confirmed by aberration-corrected transmission electron microscopy andextended X-ray absorption fine structure spectroscopy. By optimizing the preparation route (*e.g.*, one-pot syntheses involving copolymerization or in-situdoping, or post-synthetic strategies as impregnation), the family of SAHCs based on mpg-C_3N_4 has been extended to other metals (Ag,[2] Pt, and Ir). Understanding the interplay between the properties of the support (*i.e.*, porosity, composition, and structure), the identity of the metal, and its stabilization in the form of single atoms is crucial to guide the design of these unique materials. Here, we compare the effectiveness of different preparation methods, combining advanced microscopy and spectroscopy studies with density functional theory modelling to characterize the resulting materials and rationalize their observed behavior.

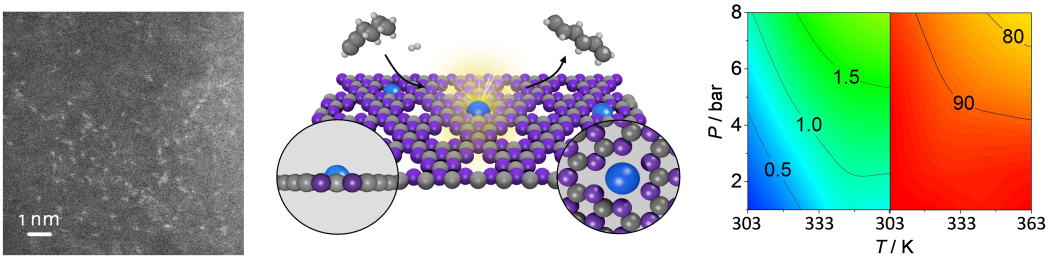


Figure 1 Aberration-corrected transmission electron micrographs confirm the presence of single Pd atoms in mpg-C_3N_4, which are thought to be stabilized within the 6-fold cavities of the carrier (as illustrated schematically), and exhibit a high reaction rate (in 10^3 $mol_{product}$ mol_{Pd}^{-1} h^{-1}) and product selectivity (in %) in the hydrogenation of 1-hexyne to 1-hexene.

G. Vilé, D. Albani, M. Nachtegaal, Z. Chen, D. Dontsova, M. Antonietti, N. López, J. Pérez-Ramírez, *Angew. Chem. Int. Ed.* **2015**, 54, 11265.
Z. Chen, S. Pronkin, T. Fellinger, K. Kailasam, G. Vilé, D. Albani, F.Krumeich, R. Leary, J. Barnard, J. M. Thomas, J. Pérez-Ramírez, M. Antonietti, D. Dontsova, *ACS Nano* **2016**, 10, 3166.

Catalytic oxidation of ethanol to acetic acid in liquid flow

S. Mostrou[1], T. Sipőcz[2], L. Kocsis[2], R. V. Jones[2], F. Darvas [2], J. A. van Bokhoven[1,3]*

[1]ETH Zürich, [2]ThalesNano Inc., [3]PSI Villigen

An environmentally friendly route to produce acetic acid is the gold-catalysed selective oxidation of bio-ethanol with molecular oxygen.[1] In conventional batch-based processes, the slow dehydrogenation of ethanol to the intermediate acetaldehyde necessitates long residence times of up to 4 hours,[2] rendering a time-consuming production and facilitating the formation of side products, like carbon dioxide and ethyl acetate. The use of a continuous-flow system comprises a smart way to overcome these process-related issues. Herein, the significantly shorter residence time within the flow reactor leads to a substantial increase of the throughput and to a comparable selectivity and conversion with the batch system. Additionally, it allows to test conditions that cannot be evaluated in a batch system due to practical and safety limitations,[3] such as the operation under atmospheric pressure and the use of concentrated ethanol solution as reactant.

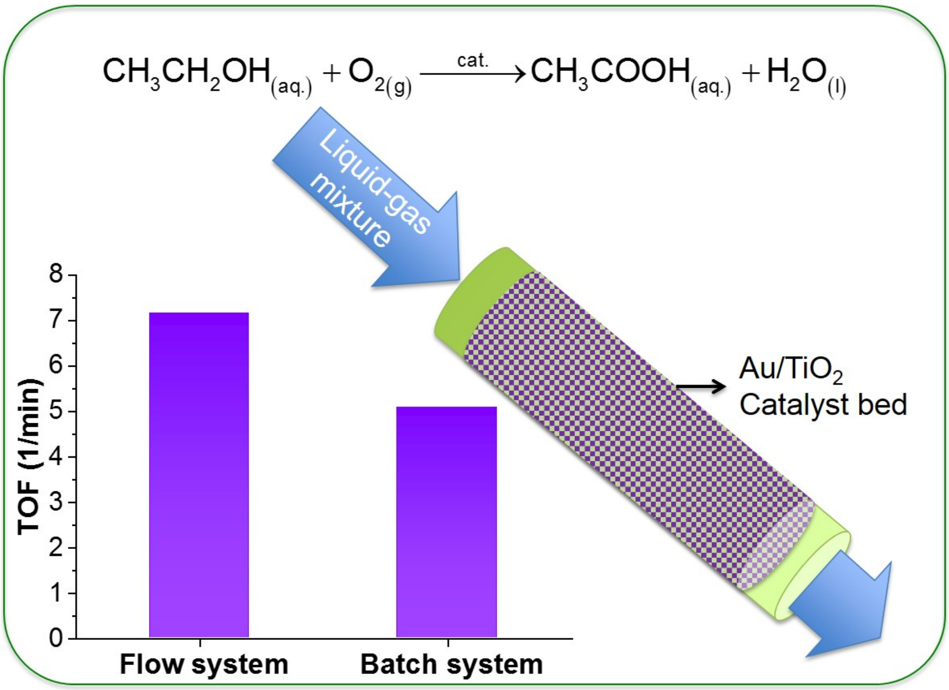


Figure 1. Illustration of the 3-phase reactor. The use of a continuous system improves turn over frequency while enhancing the safety of the operation.

[1] L. Prati, M. Rossi, J. Catal. **1998**, *176*, 552.
[2] D. Heeskens, P. Aghaei, S. Kaluza, J. Strunk, M. Muhler, Phys. Status Solidi B **2013**, *250*, 1107.
[3] C. Wiles, P. Watts, Green Chem. **2012**, *14*, 38.

Higher alcohol synthesis over modified Fischer-Tropsch catalysts

H. T. Luk[1], C. Mondelli[1], D. Curulla-Ferré[2], J. A. Stewart[2], J. Pérez-Ramírez[1]*

[1]ETH Zurich, [2]Total Research & Technology Feluy

Syngas is a key intermediate in the transformation of natural gas and coal into synthetic fuels and methanol *via* the well-known Fischer-Tropsch synthesis (FTS) and methanol synthesis (MS), respectively. The preparation of higher alcohols (HA) from syngas has also been explored since the 1930's following the fundamentally simple concept that combining MS and FTS functionalities in a single heterogeneous catalyst will enable C-C coupling and CO hydrogenation to take place simultaneously. The extent of research on this reaction has fluctuated with the oil price over the decades. Recently, the interest in exploiting unconventional (shale gas) and renewable (biomass) resources has revitalized this field.[1] Modified FTS catalysts have been studied in greater depth, in view of the feasibility to tune the HA selectivity through synergistic effects between the metals (*i.e.*, Co, Fe, Cu, or Mo).[2] Still, catalysts developed to date have not performed sufficiently well to justify the industrial implementation of a syngas-based process. Herein, we study Co- and Mo-containing catalysts, exploring the effect of the synthesis route, the metals ratio, and the reaction conditions on their performance. The establishment of structure-function relationships is targeted through the combination of advanced characterization and catalytic evaluation in order to maximize the HA yield, controlling the competitive water-gas shift (WGS) reaction, and the catalyst stability (Fig. 1).

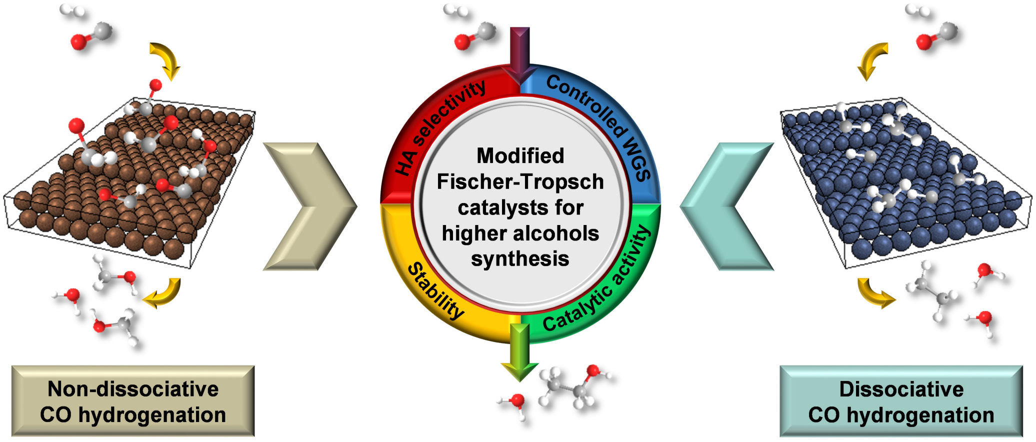


Figure 1 Schematic illustration of the potential to combine MS and FTS functionalities in a single catalyst to fulfill the four key properties for an efficient HA synthesis.

V. Subramani, S. K. Gangwal, *Energy Fuels* **2008**, 22, 814.
G. Prieto, S. Beijer, M. L. Smith, M. He, Y. Au, Z. Wang, D. A. Bruce, K. P. de Jong, J. J. Spivey, P. E. de Jongh, *Angew. Chem., Int. Ed.* **2014**, 53, 6397.

The cascade solution: solid base catalysts for the intermediate deoxygenation of bio-oil via aldol condensation

T. C. Keller[1], B. Puertolas[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich

The development of cost-efficient pathways to deoxygenate crude bio-oil is an important pre-requisite for the industrialization of biomass-derived fuels. As established methods, such as catalytic cracking or hydrodeoxygenation (HDO), are unattractive due to low carbon yields and excessive hydrogen consumption, respectively, the EU-funded CASCATBEL project targets the development of a cascade process combining pyrolysis with an intermediate catalytic deoxygenation and a subsequent HDO step. Among the different strategies for the intermediate step, including aldol condensation, esterification or ketonization reactions, we investigated the aldol condensation focussing on the design of efficient base catalysts to exploit the intrinsic reactivity of the aldehyde fraction of bio-oil for this transformation. While traditional solid bases rapidly deactivate, we report the benefits of applying siliceous zeolites incorporating atomically-dispersed alkali-[1] and alkaline-earth metals[2] to generate catalysts with moderate basicity. The optimization of the concentration and speciation of active metals is key to attain excellent activity and stability and a high selectivity in the self-condensation of propanal, which is studied as a model reaction. To evaluate the feasibility of the cascade concept, we evaluated the coupling of the aldol condensation and the HDO steps over Mo-based catalysts. Preliminary results show that the higher pressure required for HDO improves the zeolites performance (Fig. 1b), whereas the presence of hydrogen only slightly reduces the aldol condensation (Fig. 1c). Overall, a deoxygenation degree of *ca*. 70% was attained, which provides a spotlight on the viability of the cascade process.

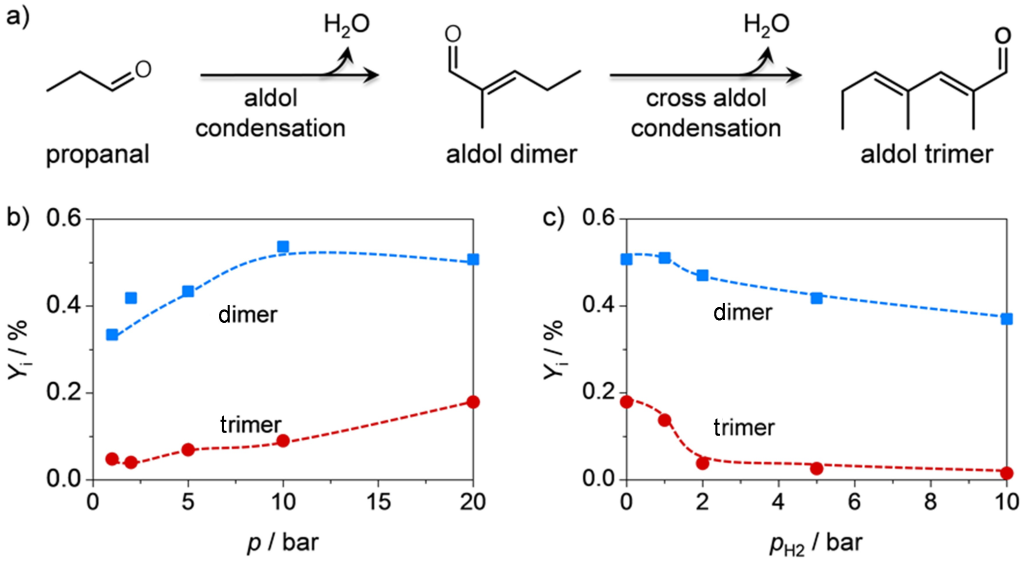


Figure 1 a) Reaction pathways for the vapor-phase conversion of propanal over base catalysts at 673 K. b) Impact of total pressure and c) partial pressure of hydrogen on the product yield over alkali metal-grafted zeolites.

1. T. C. Keller, K. Desai, S. Mitchell, J. Pérez-Ramírez, *ACS Catal*. **2015**, 5, 5388.
2. B. Puértolas, T. C. Keller, S. Mitchell, J. Pérez-Ramírez, *Appl. Catal., B* **2016**, 184, 77.

Glucose-derived platform chemicals via zeolite-catalyzed fast pyrolysis

B. Puertolas[1], Q. Imtiaz[1], C. R. Müller[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich

The production of platform chemicals such as furfural and 5-hydroxymethyl-furfural (HMF) *via* the aqueous acid-catalyzed dehydration of glucose and xylose sugars is frequently restricted by low carbon yields. To overcome this limitation, complex systems involving organic solvents or aqueous/organic biphasic mixtures and ionic liquids in combination with the use of homo- and heterogeneous catalysts have received increasing attention.[1] However, the energy-intensive solvent recovery procedure, the environmental risks associated with the sustainable handling and disposal of the chemicals involved, and the prolonged residence times required to attained reasonable yields drive the search for alternative processes. Herein, we show for the first time that the continuous gas-phase catalytic fast pyrolysis (CFP) of biomass substrates, so far exclusively used for the production of olefins and aromatics over ZSM-5 zeolites,[2] emerges as a promising technology for the selective production of furfural and HMF. Specifically, alkali metal-exchanged faujasite-type zeolites exhibit yields and selectivities as high as 15 and 90% (Fig. 1a), respectively, which has been related to the concentration of the Lewis-acid sites (Fig. 1b). Additional catalytic tests over different potassium-exchanged framework topologies evidence significant yields for beta and L zeolites, which suggests that large-pore zeolites are key to attain efficient catalysts. Being non-toxic, cheap, and easily-available, these catalytic systems are ideal candidates for an environmentally-friendly manufacture of valuable intermediates.

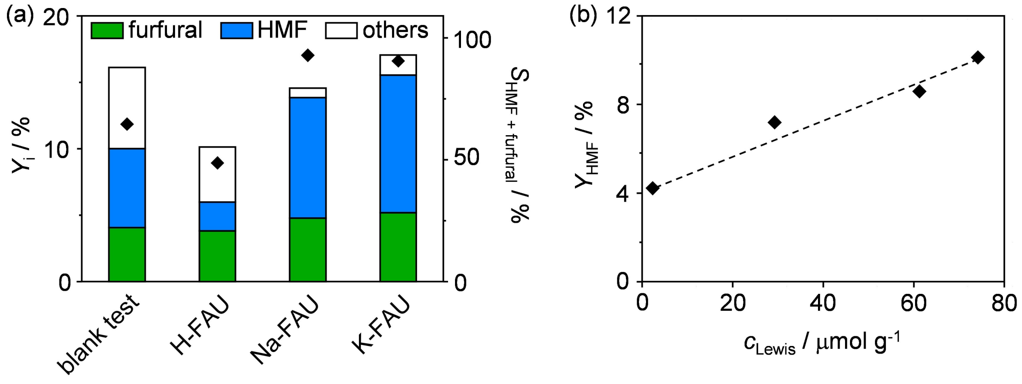


Figure 1 a) Product yields observed in the CFP of glucose over protonic and sodium- and potassium-exchanged faujasite-type zeolites. Results of the blank test are included for comparative purposes. b) Correlation between the yield of HMF and the concentration of Lewis-acid sites.

1. R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba, M. López-Grandados, *Energy Environ. Sci.* **2016**, *9*, 1144; R.-J. van Putten, J. C. van der Waal, Ed de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.* **2013**, 113, 1499.
2. Y. T. Cheng, Z. Wang, C. J. Gilbert, W. Fan, G. W. Huber, *Angew. Chem., Int. Ed.* **2012**, 51, 11097.

Exploiting the reversible segregation of Ni in redox stable La-Fe-Ni catalysts

P. Steiger[1,2], O. Kröcher[1,2], D. Ferri[1]*

[1]Paul Scherrer Institute, Villigen, [2]EPF Lausanne

Nickel is widely used as active phase in heterogeneous catalysis for its activity and relatively low cost compared to noble metals. However, current catalysts with high Ni loadings undergo microstructural changes like sintering but also degradation due to carbon deposition[1] and deactivation by sulfur species[2]. Incorporating Ni in a perovskite-type oxide (PTO, general formula: ABO_3) allows to overcome these deactivation mechanisms by exploiting the self-regenerating property of PTOs[3].

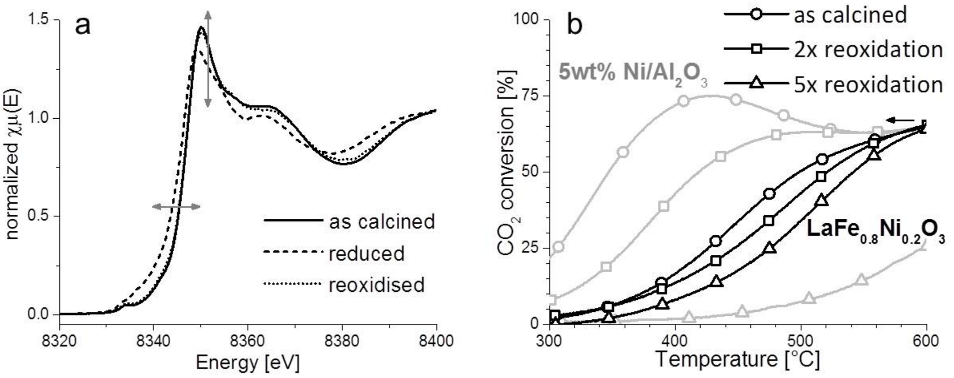


Figure 1: a) In situ Ni K-edge XANES on $LaFe_{0.8}Ni_{0.2}O_3$ during redox cycle; b) CO_2 hydrogenation after a number of simulated catalyst regeneration (reoxidation) cycles for conventional Ni/Al_2O_3 and $LaFe_{0.8}Ni_{0.2}O_3$ catalysts

The aim of the current study is to explore the structural reversibility of Ni in $LaFe_{1-y}Ni_yO_{3\pm\delta}$ for CO_2 hydrogenation and reverse water gas shift as potential applications. Nickel can be reduced and segregates from the perovskite lattice at elevated temperatures forming dispersed and active metallic Ni particles on the surface. Reoxidation allows Ni to reenter the support lattice (Figure 1a). This potentially allows C-deposits and poison species to be removed, whereas Ni sintering is prohibited and re-dispersion of the active phase on the surface upon reduction is a beneficial consequence. Catalytic activity monitored over a number of simulated catalyst regeneration-activation (i.e. redox) cycles at 600°C confirms that stability is significantly improved compared to a conventional Ni/Al_2O_3 catalyst (Figure 1b). The overall reducibility of $LaFe_{1-y}Ni_yO_{3\pm\delta}$ is directly proportional to Ni content. An important prerequisite for the reversible segregation of Ni was found to be the preservation of the perovskite lattice after reduction. The reduction temperature up to which the perovskite type lattice is preserved is lower for high Ni contents, therefore limiting the structural reversibility.

[1] C. H. Bartholomew, Catalysis Reviews, **1982**, 24, 67
[2] P. Forzatti, L. Lietti, Catalysis Today, **1999**, 52, 165
[3] Y. Nishihata, Nature, **2002**, 418, 164

Structuring hybrid Pd nanoparticles in metallic monolith channels for superior alkyne semi-hydrogenation performance in flow

D. Albani[1], G. Vilé[1], S. Mitchell[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich

Supported palladium nanoparticles modified with the hexadecyl-2-hydroxyethyl-dimethylammonium dihydrogenphosphate (HHDMA) ligand and recently commercialized under the tradename of NanoSelect^{TM} are efficient catalysts for a variety of industrially-relevant hydrogenations.To date, the performance of these hybrid materials has exclusively been assessed over loose or randomly-packed powders used in (semi-)batch or continuous mode, respectively.[1,2] This contribution explores opportunities to further enhance their performance through the macroscopic organization of the ligand-modified Pd into three-dimensional monoliths. A colloidal method is developed to firmly anchor these hybrid nanoparticles, involving the controlled deposition and calcination of a boehmite sol to form a high-surface-area *g*-Al_2O_3 washcoat and the subsequent impregnation of the active phase. The nanostructural architecture of the monolith is profiled by dedicated microscopy and sectioning techniques, confirming the uniform distribution of the washcoat layer and the palladium nanoparticles. Evaluation in the continuous-flow three-phase hydrogenation of functionalized acetylenic compounds confirms the superior selectivity and robustness of the structured catalyst with respect to the unstructured Pd-HHDMA/Al_2O_3 powder in a wide range of operating conditions (Fig. 1). Simulations undertaken for elucidating the impact of the bed isothermicity over the selectivity profile indicate that the higher thermal conductivity of the metallic monolith hinders the occurrence of unselective reactions. This is experimentally confirmed by the use of bed diluents with different thermal conductivity.

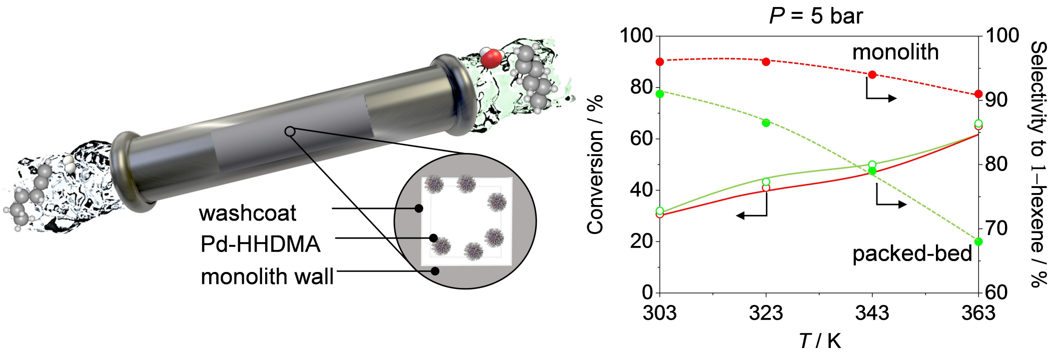


Figure 1 Illustration of the three-phase semi-hydrogenation of functionalized acetylenes over the monolithic catalyst. The plot highlights the superior selective performance of the monolith compared to a packed-bed reactor in the conversion of 1-hexyne.

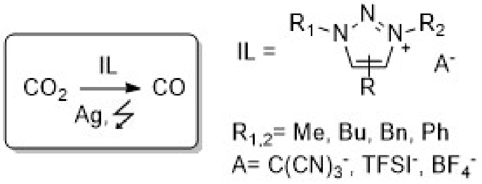
1. P. T. Witte, S. Boland, F. Kirby, R. van Maaren, B. F. Bleeker, D. A. M. de Winter, J. A. Post, J. W. Geus, P. H. Berben, *ChemCatChem* **2013**, 5, 582.
2. D. Albani, G. Vilé, S. Mitchell, P. T. Witte, N. Almora-Barrios, N. López, J. Pérez-Ramírez, *Catal. Sci. Technol*. **2016**, 6, 1621.

Triazolium-based ionic liquids for electrochemical reduction of CO_2

D. Vasilyev[1], P. Dyson[1]*

[1]EPF Lausanne

The electrochemical transformation of carbon dioxide to valuable products has recently attracted a lot of attention [1-3]. Ionic liquids, employed with metal electrodes, suppress the hydrogen evolution side reaction (HER) and significantly decrease the overpotential for CO_2 reduction [4]. In current project the triazolium-based ionic liquids were employed instead of the conventional imidazolium ones. They possess high catalytic performance, selectively reducing carbon dioxide to CO on silver electrode. This high performance along with high stability and low viscosity and synthetic availability makes them an attractive option for CO_2 transformation.



[1] Qiang Liu, Lipeng Wu, Ralf Jackstell, Matthias Beller *Nature Commun.*, **2015**, 6:5933
[2] Jinli Qiao, Yuyu Liu, Feng Hong, Jiujun Zhang *Chem. Soc. Rev.*, **2014**, 43, 631–675
[3] Rem Jem Lim et al. *Catalysis Today*, **2014**, 233, 169–180
[4] Brian A. Rosen et al. *Science*, **2011**, 334, 643–644

Structure-performance relations in the semi-hydrogenation of acetylene over indium oxide

D. Albani[1], O. Martin[1], G. Vilé[1], S. Mitchell[1], N. López[2], J. Pérez-Ramírez[1]*

[1]ETH Zurich, [2]ICIQ

The partial hydrogenation of alkynes is a crucial step for the purification of olefin streams in the petrochemical industry. Conventionally, this reaction is conducted over palladium nanoparticles supported on *a*-Al_2O_3. However, the catalyst needs to be heavily promoted, often using toxic modifiers, to prevent undesirable over-hydrogenation and oligomerization pathways. The recent discovery that CeO_2 catalyzes this family of reactions with outstanding selectivity[1] has kindled renewed interest in oxidic materials for alkyne hydrogenation. Inspired by the remarkable performance of bulk In_2O_3 in the hydrogenation of CO_2 to methanol,[2] we explored the potential of this oxide for the partial hydrogenation of acetylene to ethylene. Interestingly, this catalyst demonstrates 80% selectivity to ethylene at full conversion and ambient pressure (Fig. 1a). Differently from ceria, detailed analyses by temperature-programmed reduction with H_2 (H_2-TPR), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and density functional theory (DFT) link the excellent hydrogenation performance with a surface reconstruction during the reaction leading to the formation of metallic indium (In_3) clusters (Fig. 1b). Various pretreatments were studied to rationalize the structural changes observed upon exposure to different reducing agents (CO and H_2), enabling the derivation of structure-performance relations.

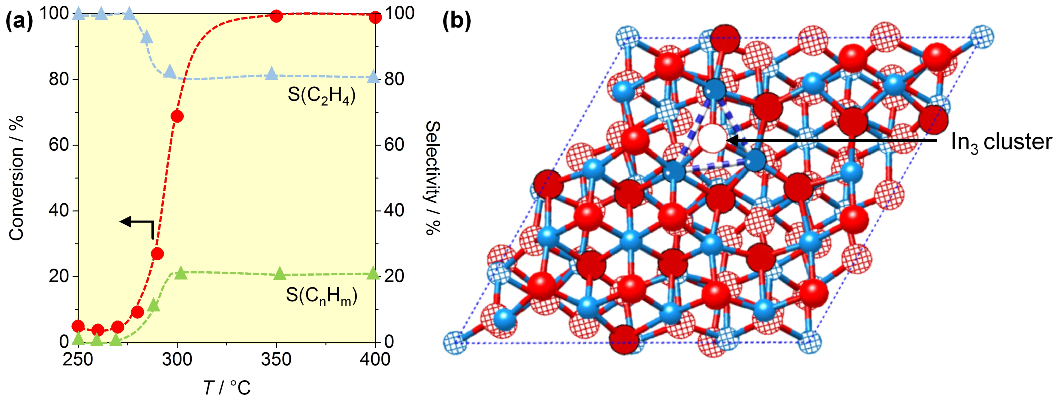


Figure 1 (a) Conversion (red) and selectivity to ethylene (blue) and to oligomers (green) in the gas-phase semi-hydrogenation of acetylene over In_2O_3. (b) Illustration of the In_2O_3 structure after surface reduction. Color code: oxygen (red), indium (blue).

1. G. Vilé, B. Bridier, J. Wichert, J. Pérez-Ramírez, *Angew. Chem. Int. Ed.* **2012**, 51, 8620.
2. O. Martin, A.J. Martín, C. Mondelli, S. Mitchell, T.F. Segawa, R. Hauert, C. Drouilly, D. Curulla-Ferré, J. Pérez-Ramírez, *Angew. Chem. Int. Ed.* **2016**, 55, 6261.

The Significance of Lewis Acid Sites for the Selective Catalytic Reduction of Nitric Oxide on Vanadium-Based Catalysts

A. Marberger[1,2], D. Ferri[1], M. Elsener[1], O. Kröcher[1,2]

[1]Paul Scherrer Institut – 5232 Villigen, [2]Institute of Chemical Sciences and Engineering, EPFL - 1015 Lausanne

The selective catalytic reduction (SCR) with NH_3 is the most efficient after treatment technology for reducing nitrogen oxides emissions from stationary and mobile sources. The proposed reaction mechanisms on V-based catalysts indicate that the surface acid sites are responsible for the adsorption of NH_3, which then reacts with NO according to an Eley-Rideal mechanism. Brønsted acids sites were proposed as active centers by Topsøe [1], whereas Ramis et al. [2] considered Lewis centers as the active species. Spectroscopic studies reported various evidences in support of either one of the mechanisms. However, they often exhibit limitations with respect to the time scale of observations and reaction conditions. In this study, we followed the SCR reaction using time-resolved DRIFTS and DR-vis spectroscopy combined with modulation excitation spectroscopy [3] on a 2.0 wt% V_2O_5/10 wt% WO_3/TiO_2 SCR catalyst calcined at 450°C for 10 h.

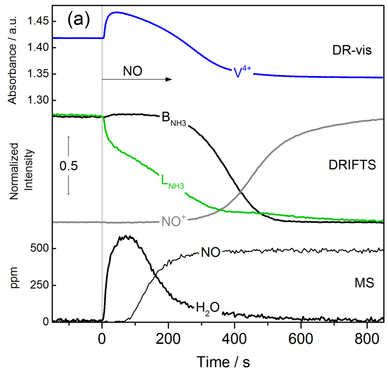


Figure 1:
Temporal response of signals from DRIFT and DR-vis spectra and online MS obtained while flowing 500 ppm NO on 2 wt% V2O5-10 wt% WO3-TiO2 after equilibration with 500 ppm NH3 (adsorption/ desorption) at 250°C.

Time-resolved DRIFT spectroscopy allowed continuous monitoring of the crucial adsorbed species during NO addition after NH_3 adsorption/desorption at 250°C (Figure 1). While ammonia coordinated to Lewis acid sites (L_{NH3}, 1603 cm^{-1}) reacted immediately, the NH_4^+ species on Brønsted acid sites (B_{NH3}, 1423 cm^{-1}) started decreasing only after 200 s. Identical experiments with 1 vol% H_2O in the gas mixture revealed the same behavior but at lower intensity levels. Upon NO addition, the online analysis showed the evolution of H_2O in coincidence with the consumption of the L_{NH3} species. The ratio of formed H_2O to consumed NO was 1.53, closely matching the stoichiometry of the SCR reaction. The identical DR-vis experiments exhibited an immediate increase of V^{4+} contribution before returning to higher levels of V^{5+} in a continuous $NO+O_2$ feed.

The *operando* DRIFTS and DR-vis study together with the phase modulation approach sets the standard SCR mechanism into a new perspective. It was shown that for a typical V-based SCR catalyst at low temperature, NO predominantly reacts with L_{NH3}. The B_{NH3} is extraneous to the SCR reaction and possibly only serves as a NH_3 reservoir. Furthermore, L_{NH3} is coordinated to V^{5+}, which only together with NO reduces to V^{4+}. To this end, it was experimentally proven that the NH_2NO intermediate is formed during the reduction of the Lewis V^{5+} active center.

These findings provide important information concerning the design of future catalysts. A catalyst with Lewis centers in the desired oxidation state (and likely coordination) should be anticipated to enhance the performance of V-based SCR catalysts in the low temperature regime.

[1] Topsøe, N.-Y. *Science* **1994**, *265*, 1217-1219
[2] Ramis, G.; Busca, G.; Bregani, F.; Forzatti P. *Appl. Catal.,* **1990**, *64*, 259-278
[3] Baurecht, D.; Fringeli, U.P. *Rev. Sci. Instrum.*, **2001**, *72*, 3782-3792

Controlling the selectivity to chemicals from lignin via catalytic fast pyrolysis

Z. Ma[1], V. Custodis[1], A. Ghosh[2], J. A. van Bokhoven[1,3]*

[1]ETH Zurich, [2]SABIC Americas, [3]Paul Scherrer Institute, Villigen

1. Introduction: Due to the worldwide demand for renewable energy, lignocellulosic biomass becomes more and more attractive as feedstock for the production of fuels and commodity chemicals. Lignin depolymerization with selective bond cleavage remains a major challenge for selectively converting it into liquid hydrocarbons and other value-added chemicals. Furthermore lignin produces more coke/char than other components in biomass: cellulose and hemicellulose. The use of catalysts may overcome these problems and thus provide a solution for lignin conversion to valuable chemicals. In this work, the opportunities of catalysis for tuning the selectivity for lignin conversion by catalytic fast pyrolysis over different catalysts, such as zeolites, transition metal oxides, and supported transition metals, will be discussed.

2. Results and discussion: Scheme 1 shows a general reaction scheme for lignin non-catalytic and catalytic fast pyrolysis. It identifies the role of catalysis and the partial control of the selectivity to the final products. The most abundant compounds in the liquid fraction over different catalysts are indicated. Under non-catalytic fast pyrolysis conditions, lignin decomposes under heat and generates depolymerization products, following a radical reaction mechanism. These radicals are highly reactive and can rapidly repolymerize to form undesired solid or be stabilized to form stable products, such as phenols alkoxy and phenols. Over transition metal oxides, alkoxy phenols are the main products, however, the relative ratio between oxygenated compounds varies significantly. Over zeolite-supported cobalt and nickel catalysts, the formation of aromatic hydrocarbons is enhanced. The intermediates are stabilized by adsorption in the pores in the presence of porous materials without acidic function, such as silicalite, thus increasing the yield of liquid without changing the liquid products distribution. In the presence of strong acidic zeolites, such as H-USY and H-ZSM5 with low Si to Al ratio, complex reactions are involved, such as dehydration, decarboxylation, dealkylation, cracking, isomerization, oligomerization, etc. Aromatic hydrocarbons are the final products of such transformations. Phenols are intermediate products, the amount of which can be controlled to some extent by modification of the acid function and by introduction of transition metals, such as molybdenum and iron into the acidic zeolites.

3. Conclusions: Generally, the selectivity varies strongly with the type of lignin and reaction conditions, which poses many challenges. Overall various valuable compounds with high yield can be produced selectively by choosing the appropriate catalysts and reaction conditions. In exceptional cases the selectivity is directed to a single product, such as vanillin over copper oxide (max. selectivity ~31%) and guaiacol over nickel oxide (~25%). The results indicate that there is significant potential for changing product selectivity by varying the catalyst and reaction conditions. However, significant efforts should be devoted to the development of new catalyst and catalytic system, study of the mechanism by model compounds, as well as the engineering aspects of the process.

1. G. W. Huber, S. Iborra, A. Corma,*Chem. Rev.***2006**, 106, 4044-4098.
2. C. Zhao, Y. Kou, A. A. Lemonidou, X. Li, J. A. Lercher,*Angew. Chem. Int. Ed.***2009**, 48, 3987-3990.
3. J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen,*Chem.Rev.***2010**, 110, 3552-3599.
4. Z. Ma, E. Troussard, J. A. van Bokhoven,*Appl. Catal.A***2012**, 423-424, 130-136.
5. Z. Ma, V. Custodis, J. A. van Bokhoven,*Catal.Sci. Tech.***2014**, 4, 766-772.

Quantifying the complex pore architecture of hierarchical faujasite zeolites and the impact on diffusion

R. Warringham[1], T. C. Keller[1], P. Crivelli[1], J. Kenvin[2], M. Sterling[2], J. J[2], S. Mitchell[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich, [2]Micromeritics Instruments Corporation

An exact knowledge of the architecture of complex pore networks and the impact on transport processes is critical to understand and optimize their integration in many functional solids, including catalysts, fuel cells, batteries, and sorbents.[1] Advanced characterization methods and techniques which can yield such a quantitative assessment of these porous materials are integral in achieving a deeper level of understanding how the pore network relates to function. In this contribution, we demonstrate a robust and versatile approach to quantitatively map pore constrictions within hierarchical faujasite-type (Y and USY) zeolites, the most widely applied zeolitic materials in industry. Differential hysteresis scanning (DHS) measurements by high-resolution argon sorption, coupled with an advanced modelling framework, enable the derivation of the amount and size of pyramidal, constricted, and occluded mesopores.[2] An example of a contour plot derived by the DHS of argon sorption is presented in Fig. 1a, where the regions of intensity are attributed to distinct mesopore geometries. Such an approach yields unprecedented insight into the impact of widely practiced demetallation treatments on the porosity evolution and clearly highlights the interplay between the geometry of mesopores developed by a given treatment. Based on the findings, the dynamic assessment by positron annihilation lifetime spectroscopy (Fig. 1b) confirms the effectiveness of each mesopore type at enhancing the diffusion of the *ortho*-positronium probe molecule within the crystal. The quantitative descriptors attained by these complementary techniques can revolutionize the design of porous materials for a wide range of applications.

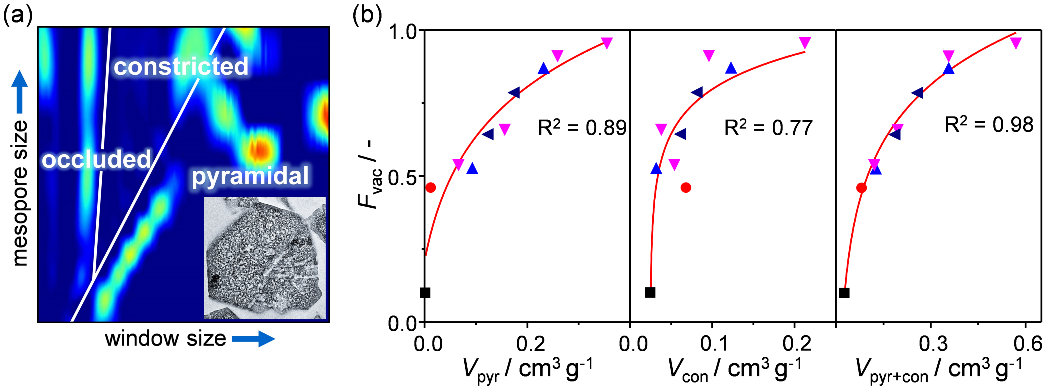


Figure 1 (a) An example contour plot derived by DHS of argon sorption and (b) the correlation between the mesopore geometry and the effectiveness, based on the out-diffusion of *ortho*-positronium (F_{vac}).

1. a) Y. Li, Z.-Y. Fu, B.-L. Su, *Adv. Funct. Mater*. **2012**, 22, 4634; b) S. Mitchell, A. B. Pinar, J. Kenvin, P. Crivelli, J. Kärger, J. Pérez-Ramírez, *Nat. Commun*. **2015**, 6:8633.
2. J. Kenvin, S. Mitchell, M. Sterling, R. Warringham, T. C. Keller, P. Crivelli, J. Jagiello, J. Pérez-Ramírez, *Adv. Funct. Mater.* **2016**, doi:10.1002/adfm.201601748.

Monitoring pore evolution during the detemplation of zeolite catalysts by positron annihilation spectroscopy

R. Warringham[1], A. Zubiaga[1], L. Gerchow[1], P. Crivelli[1], S. Mitchell[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich

Organic structure directing agents (SDA) are commonly employed in the synthesis of zeolite materials, particularly in the synthesis of high-silica zeolites. An example of such a SDA is tetrapropylammonium (TPA$^+$) which is widely applied in the manufacture of MFI-type zeolites (Fig. 1a) and are subsequently removed *via* calcination. However, detailed insight into the porosity evolution as a function of the template removal is scarce due to the lack of sensitive characterization methods. Positron annihilation spectroscopy (PAS) is ideally suited for such measurements as the probe molecule (positronium, Ps) forms uniformly within the bulk of the material and actively diffuses towards larger open volumes with a finite lifetime.[1] This enables the dynamic assessment of the connectivity of the micropores within zeolite crystals, providing insight into voids inaccessible to routinely used techniques as gas sorption, in which the probe molecule can only access voids accessible from the external surface. Here, we report the application of PAS to study the removal of TPA$^+$ from MFI zeolites of different crystal size and composition. Gas sorption and thermogravimetric analysis confirm the stepwise removal of the template upon calcination for different durations under isothermal conditions. Interestingly, Ps are seen to be trapped within the micropore structure until the very last stages of detemplation, suggesting the formation of template-free volumes within the crystal bulk (Fig. 1b). Based on additional information obtained by confocal fluorescence microscopy, a mechanism for template removal in the context of Ps diffusion is proposed (Fig. 1c).

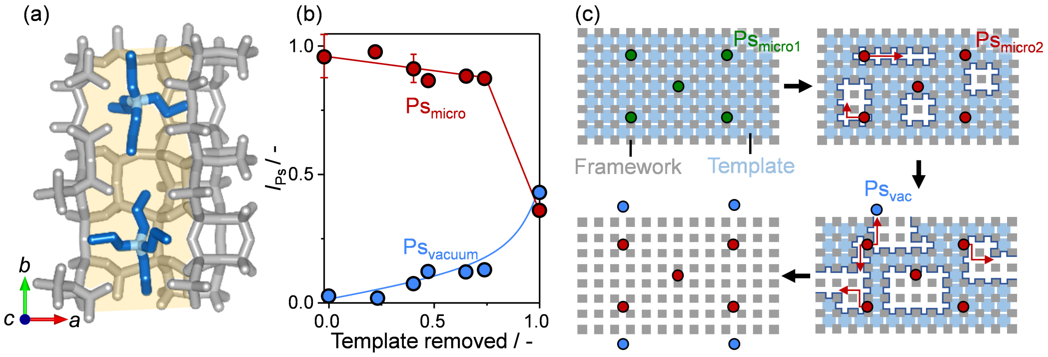


Figure 1 (a) Location of TPA$^+$ within the straight pore channels of a ZSM-5 zeolite, (b) the distribution of Ps components as a function of the template removal, (c) a possible mechanism for the SDA removal based on the insights gained by PAS.

1. (a) D. W. Gidley, H. G. Peng, R. S. Vallery, *Ann. Rev. Mat. Res.* **2006**, 36, 49; (b) M. Milina, S. Mitchell, D. Cooke, P. Crivelli, J. Pérez-Ramírez, *Angew. Chem., Int. Ed.* **2014**, 54, 1591.

CO activation on supported Pt single-atom catalysts: a density functional theory study

X. Wang[1,2], D. Palagin[2], J. A. van Bokhoven[1,2]

[1]ETH Zurich, [2]Paul Scherrer Institut

Supported platinum catalysts show high activity and excellent stability in the low temperature carbon monoxide oxidation and water-gas shift reactions that are important for a wide range of applications, such as fuel cell design or automotive emission control [1]. However, no consensus on the catalytic mechanisms and atomic configurations of the active sites has been reached. In particular, the size of the catalytically active Pt nanoparticles, and, more specifically, whether platinum single atoms can act as active catalytic sites, remains an open question [2]. Although vibrational spectroscopy can be used to differentiate and quantify the active sites, the vast configurational manifold of the supported metal catalyst makes it difficult to precisely correlate vibrational spectra to particular structures [3]. Aiming at a detailed atomistic insight into the nature of the active sites, density functional theory is used to study the possibility of activation of a CO molecule adsorbed on a range of supported single-atom platinum catalysts, including Pt/CeO_2, Pt/SiO_2, $Pt/\gamma\text{-}Al_2O_3$, Pt/TiO_2, and Pt/ZrO_2. Comparison to experimentally observed carbon-oxygen stretch frequencies is used to verify the potential catalytic activity of single platinum atoms and to assign the observed vibrational modes to their respective geometrical structures. The effects of a particular support surface and an adsorption site are discussed.

[1] An K, et al. Journal of the American Chemical Society, 2013, **135**, 16689.
[2] Qiao Botao, et al. Nature chemistry, 2011, **3**, 634.
[3] Ding Kunlun, et al. Science, *2015,* **350,** 189.

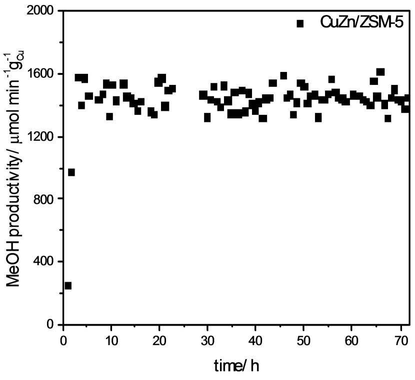
Highly selective and stable copper-zinc catalyst for carbon dioxide hydrogenation of methanol

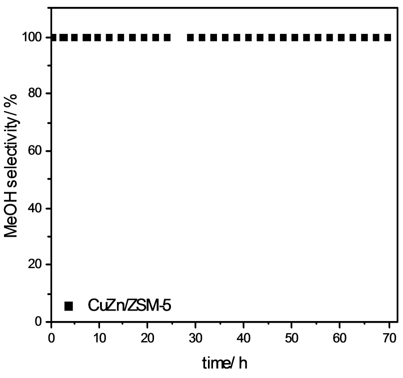
J. Lee[1], S. Saedy[1], M. Ranocchiari[1], J. A. van Bokhoven[2,1]*

[1]Paul Scherrer Institute, [2]ETH Zurich

Methanol is a pivotal compound in the chemical industry as a building block of numerous chemicals. In addition, it is an energy storage material.[1] The sustainable methanol synthesis via carbon dioxide hydrogenation has a great advantage in utilizing a greenhouse gas to produce useful chemical materials. Carbon dioxide hydrogenation to methanol requires an efficient catalyst due to the high thermodynamical stability of carbon dioxide. Despite high methanol productivity, the traditional Cu/ZnO/Al_2O_3 catalyst suffers from low stability and selectivity which originates from poor water resistance. Moreover, it produces a large amount of carbon monoxide.[2, 3] The interface between copper and zinc atoms plays a critical role in selective production of methanol.[4]

Here, we present the copper-zinc catalyst supported on zeolite, which showed excellent methanol selectivity and high durability in carbon dioxide hydrogenation. The methanol selectivity of the catalyst continuously enhanced during reaction and finally provided complete selectivity at ca. 1 % carbon dioxide conversion level. The high selectivity was only observed on zeolite supported catalyst Aluminum oxide and silicon oxide as support yielded low selectivity. The catalyst also exhibited constant methanol production with perfect selectivity over the tested 72 h of reaction. The stable morphology of copper-zinc nanoparticles, and zeolite crystal structure measured by TEM and *in situ* XRD ensured the stable catalytic performance.





[1] M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709-1742.
[2] F. Arena, K. Barbera, G. Italiano, G. Bonura, L. Spadaro, F. Frusteri, *J. Catal.* **2007**, *249*, 185-194.
[3] E. L. Kunkes, F. Studt, F. Abild-Pedersen, R. Schlögl, M. Behrens, *J. Catal.* **2015**, *328*, 43-48.
[4] A. Le Valant, C. Comminges, C. Tisseraud, C. Canaff, L. Pinard, Y. Pouilloux, *J. Catal.* **2015**, *324*, 41-49.

Cobalt-Nickel Spinels and Doped Manganese Oxides as Water Oxidation Catalysts

M. Olah[1], G. R. Patzke[1]

[1]University of Zurich

In the course of our ongoing studies on manganese oxides as water oxidation catalysts (WOCs), we focused our research on Mn_2O_3,[1] which showed the best catalytic activity. The influence of different dopants (Fe, Co, Ni, Cu) on the WOC activity of this matrix was studied.

In parallel, cobalt-nickel spinels were investigated as WOCs. Recently, *Tüysüz* et *al.*[2] reported enhanced catalytic activity in electrochemical water oxidation by incorporation of Fe into Co_3O_4 spinel. Furthermore, Ni doping has been shown to improve the activity of CoCNC carbodiimides.[3] Inspired by these results, we started investigating the influence of Ni doping on the water oxidation activity of Co_3O_4. The materials were synthesized by co-precipitation method according to ref. [4]. The obtained materials were tested as photocatalytic WOCs using $[Ru(bpy)_3]^{2+}$ as photosensitizer and $Na_2S_2O_8$ as sacrificial electron acceptor at different catalytic conditions.

Catalyst design for methane oxyhalogenation - comparison between chlorine and bromine chemistry

G. Zichittella[1], V. Paunovic[1], N. Aellen[1], A.P. Amrute[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich

The selective conversion of methane, the major component of natural gas, into value-added chemicals is one of the greatest challenges in modern catalysis research. Oxyhalogenation has emerged as an appealing route to functionalize the alkane under mild conditions.[1] Our recent work revealed that *in situ* integration of surface-catalyzed HBr oxidation with gas-phase methane bromination is key to achieve selectivities of the desired CH_3Br as high as 95% on a vanadium phosphate (VPO) catalyst.[1] The present work targets the establishment of catalyst design criteria for methane oxychlorination and oxybromination, and understanding of the fundamental differences of halogen chemistry in these reactions over metal oxides and phosphates. Oxide catalysts require lower reaction temperature in oxychlorination than in oxybromination due to their efficiency in activating HCl and to the higher reactivity of chlorine than bromine in the gas phase. In contrast, the mild oxidizing phosphate catalysts are active in oxychlorination at higher temperatures than in oxybromination due to their difficulty in activating HCl (Fig. 1a). At a similar level of conversion, the selectivity to monohalomethanes over the same oxide catalyst was comparable in both reactions, but the formation of CO_x was more pronounced in oxybromination due to the higher operating temperature and reactivity of bromomethanes. The opposite trend was observed over phosphate catalysts, since the high temperature needed for chlorine evolution leads to combustion of chloromethanes. Nevertheless, the selectivity to halomethanes is strongly dependent on the H*X* partial pressure over oxides, particularly in case of oxybromination (Fig. 1b). This is attributed to the higher affinity of bromine for the oxide surface compared to chlorine, which leads to enhanced halogen coverage at high partial pressure of HBr, and a better suppression of combustion reactions than in the case of oxychlorination.

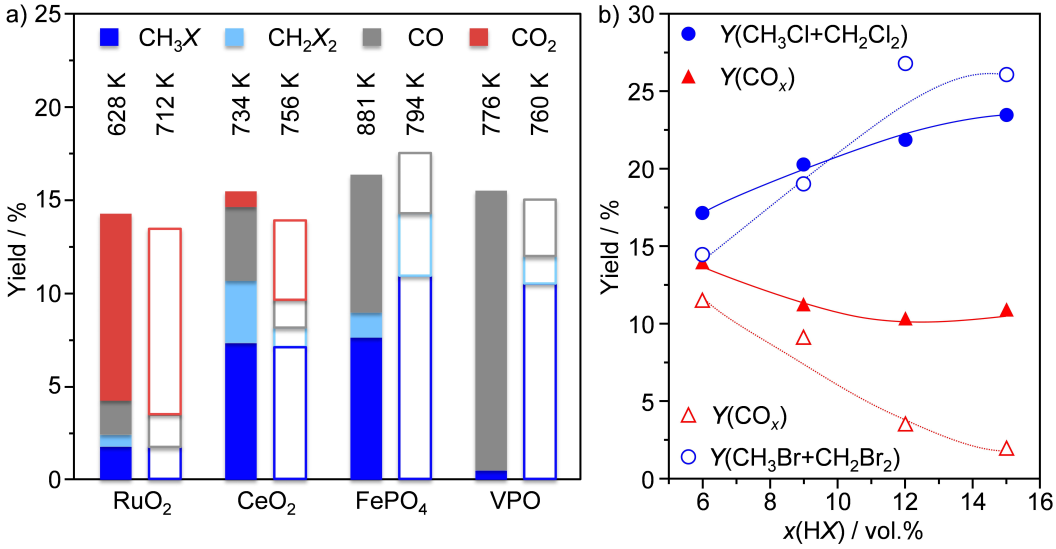


Figure 1 a) Catalytic performance of oxide and phosphate materials in methane oxychlorination (filled bars) and oxybromination (empty bars) in the presence of 6 vol.% H*X*. b) Methane oxychlorination (filled symbols) and oxybromination (empty symbols) on CeO_2 at different H*X* volumetric fraction (*x*) at 773 K.

1. V. Paunović, G. Zichittella, M. Moser, A. P. Amrute, J. Pérez-Ramírez, *Nat. Chem.* **2016**, doi: 10.1038/nchem.2522.

Mechanism of bifunctional ceria in vinyl chloride manufacture from ethylene

M. Scharfe[1], M. Capdevila[2], A.P. Amrute[1], V. Paunovic[1], D. Teschner[3], L. Szentmiklósi[4], M. Jankowski[5], J. Drnec[5], N. López[2], J. Pérez-Ramírez[1]*

[1]ETH Zurich, [2]ICIQ, [3]Fritz Haber Institute, Max Planck Society, [4]Institute of Isotopes, [5]ESRF

The manufacture of polyvinyl chloride (PVC) relies on the production of vinyl chloride (VCM) *via* a two-step process comprising ethylene oxychlorination to ethylene dichloride (EDC) on intrinsically unstable cupric chloride catalysts and a subsequent energy-intensive thermal cracking. Recently, we demonstrated that ceria performs stably as a bifunctional catalyst enabling ethylene oxychlorination on redox sites to EDC, which is subsequently dehydrochlorinated on acid centers to VCM in 21% yield (Fig. 1a).[1] To gain deeper understanding of the reaction mechanism, we combine kinetic testing, advanced characterization, and Density Functional Theory (DFT) simulations on CeO_2. *In situ* Synchrotron XRD (SXRD) suggests that changes only occur in surface-near layers (Fig. 1b). Prompt Gamma Activation Analysis (PGAA) evidences that a high chlorine coverage is beneficial for preserving a high selectivity to desired products (EDC, VCM) by suppressing side reactions to CO_x and over-chlorinated products, like dichloroethene (DCE) (Fig. 1c). Since acidity was shown to be a prerequisite for VCM selectivity,[1] determination of the exact nature of acid sites in as-prepared and stabilized samples is targeted by solid state NMR spectroscopy with probe molecule, such as trimethylphospine, adsorption. DFT analysis predicts a local lattice parameter increase when Ce^{3+} atoms are formed through oxygen abstraction and/or chlorination, which is in line with SXRD. Transition state search indicates that ceria, apart from being able to dissociate HCl, acts as both a Brønsted and Lewis acid/base pair for proton and electron exchange, respectively, during several steps of the reaction. Energy barriers for the formation of the versatile intermediates will be derived to identify the most probable pathways and indicate the way how to tune the surface to attain the highest VCM selectivity.

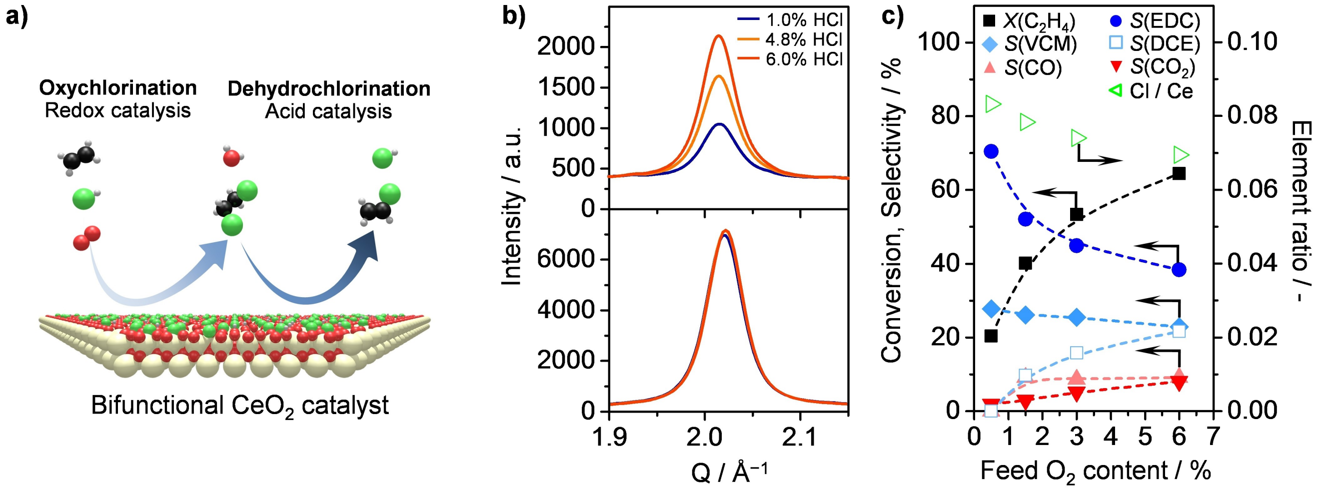


Figure 1 a) Bifunctional ceria integrates both oxychlorination and dehydrochlorination functions on a single surface for direct VCM production. b) Excerpt of *in situ* SXRD patterns of CeO_2 surface near layers (top) and bulk (bottom). c) Conversion, selectivity, and Cl/Ce ratio *versus* oxygen content in an *operando* PGAA experiment on CeO_2.

1. M. Scharfe, P. A. Lira-Parada, V. Paunović, M. Moser, A. P. Amrute, J. Pérez-Ramírez, *Angew. Chem., Int. Ed.* **2016**, *55*, 3068.

Europium oxide - a highly selective catalyst for one-step vinyl chloride production from ethylene

P. A. Lira-Parada[1], M. Scharfe[1], A.P. Amrute[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich

The PVC business relies on the efficient manufacture of the vinyl chloride monomer (VCM). The two-step production process for the latter, involving ethylene oxychlorination on supported copper chloride followed by unselective thermal cracking, suffers from severe stability issues. Thus, aiming at improving and intensifying the existing technology by the direct production of VCM from ethylene over a stable material, we investigated the performance of lanthanide oxides, since their mild reducibility and high acidity can be envisaged to suppress overoxidation and favor *in situ* dehydrochlorination of ethylene dichloride (EDC) to VCM, respectively. Our initial efforts in this direction resulted in the identification of ceria attaining 40% VCM and 34% EDC selectivity at high ethylene conversion.[1] A wider screening of lanthanide-based catalysts demonstrated Eu_2O_3 as a superior catalytic system, displaying a significantly higher selectivity to VCM (›75%) at reasonable conversion level compared to other materials (Fig. 1a). Characterization of used samples demonstrated that the original europium oxide phase transformed into europium oxychloride, as is also the case for other lanthanides, except for CeO_2 which preserved its oxidic form (Fig. 1b). Improved understanding of the catalyst structure was gained through advanced characterization, ultimately enabling the establishment of structure-performance relationships. Furthermore, we showed that industrially appealing VCM yields can be achieved through the tuning of reactor configurations and/or by synthesizing mixed oxides of europia and ceria.

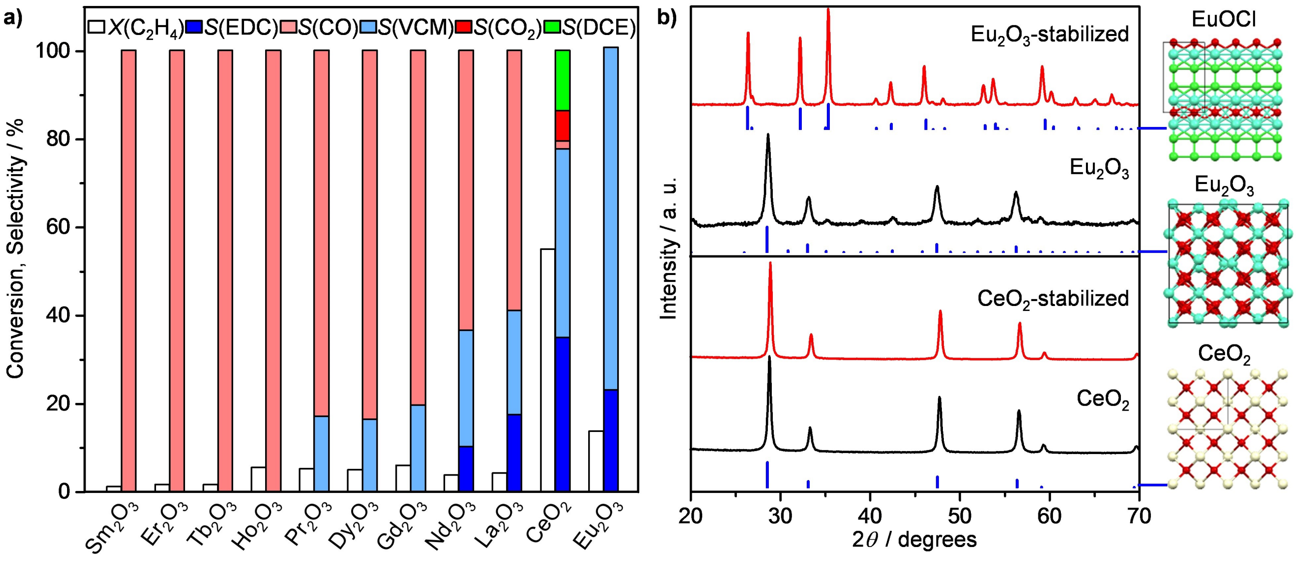


Figure 1 a) Performance of lanthanide oxides in ethylene oxychlorination at 723 K. b) X-ray diffractograms of as-prepared and stabilized CeO_2 and Eu_2O_3 catalysts.

1. M. Scharfe, P. A. Lira-Parada, V. Paunović, M. Moser, A. P. Amrute, J. Pérez-Ramírez, *Angew. Chem., Int. Ed.* **2016**, 55, 3068.

One-pot conversion of aliphatic carboxylic acids to linear alpha olefins through tandem hydrogenation/dehydration

J. Yeap[1], B. Rozmysłowicz[1], J. Luterbacher[1]*

[1]EPF Lausanne

Linear alpha olefins (LAO) are straight-chained hydrocarbons with terminal unsaturation, and are commonly used industrially in the production of plastics. Having a double bond at the end of the hydrocarbon chain makes it highly prized in polymerization reactions due to its use in producing oligomers of targeted lengths. A common way of producing LAOs is through ethylene oligomerization over a nickel catalyst.[1] The drawback of this process is that only LAOs with an even number of carbons can be produced, and is ultimately unsustainable due to the use of fossil-based ethylene.

In contrast, biomass represents an attractive feedstock of sustainable carbon. Specifically, biomass-derived carboxylic acids could be an interesting starting material for the production of LAOs. Carboxylic acids are abundant in nature in the form of vegetable oils and can easily be produced from biomass by microbial conversion.[2] The main challenge is the deoxygenation of the relatively stable carboxylic acids to LAOs while preventing branching or isomerization of the double bond.

In the present study, we explore the one-pot catalytic conversion of aliphatic carboxylic acids to LAOs via tandem hydrogenation/dehydration reactions. A variety of short chain linear carboxylic acids are effectively converted to LAOs under a H_2 atmosphere, in both aqueous and organic solvents. The reaction was carried out in flow conditions at low temperatures. We plan to combine this system with the microbial production of carboxylic acids from biomass to have an integrated platform for the production of biomass-derived LAOs.

[1] E. F. Lutz, *J. Chem. Educ.* **1986**, *63*, 202.
[2] E. J. Steen, Y. Kang, G. Bokinsky, Z. Hu, A. Schirmer, A. McClure, S. B. del Cardayre, J. D. Keasling, *Nature* **2010**, *463*, 559.

Chemical Layer Deposition of metal oxide overcoats with targeted porosity by Stoichiometric and Kinetic control

B. P. Le Monnier[1], F. Héroguel[1], J. Luterbacher[1]*

[1]EPF Lausanne

Catalyst overcoating could become an important strategy in catalyst synthesis due to the possibility of tuning surface reactivity, active site stability and general physicochemical properties of the materials.

It has been demonstrated that overcoating via Atomic Layer Deposition (ALD) and subsequent calcination to induce porosity in the overcoat is an effective catalyst stabilization technique [1]. However, this process is known to be expensive and difficult to apply to powders. Using sol-gel chemistry could be an attractive approach but batch deposition approaches often suffer from poor control of the resulting nanomaterial especially in the case of highly reactive oxide precursors such as aluminum alkoxides..

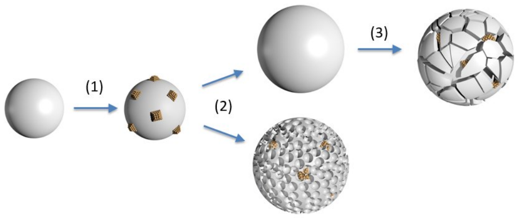


Fig. 1: Steps of catalyst preparation: (1) Impregnation, (2) overcoating, (3) thermal treatment

We report a strategy that combines the advantages of ALD and sol-gel chemistry techniques by applying a solution-phase layer-by-layer technique controlled by the stoichiometry and kinetics of precursor deposition. Our procedure allows for the synthesis of overcoats with targeted thickness and porosity by judiciously choosing synthesis parameters such as water/alkoxide ratio, solvent choice or material aging conditions. Our initial study focused on the overcoating of an alumina supported copper catalyst (Fig. 1). The texture of the overcoats was analyzed by N2-physisorption and copper accessibility was measured by N2O titration and the shape of the coating was imaged by STEM-HAADF. Because this layer-by-layer coating method is performed in solution, a vast number of parameters can be controlled compared to gas phase deposition potentially leading to the formation of several novel nano-environments.

[1] Brandon J. O’Neill, David H. K. Jackson, Jechan Lee, Christian Canlas, Peter C. Stair, Christopher L. Marshall, Jeffrey W. Elam, Thomas F. Kuech, James A. Dumesic, and George W. Huber, ACS Catal. **2015**, 5, 1804−1825

Identification of the Active State of Platinum and the Role of Alkali Metal Promotion in Water-Gas Shift over Supported Pt Catalysts

K. Roy[1,3], L. Artiglia[2], T. Huthwelker[2], J. A. van Bokhoven[1,3]*

[1]Institute for Chemical and Bioengineering, ETH Zürich, 8093 Zürich, Switzerland, [2]Swiss Light Source, Paul Scherrer Institut, 5232 Villigen, Switzerland, [3]Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institut, 5232 Villigen, Switzerland

Water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) is an important reaction to obtain clean hydrogen from natural gas feedstock for fuel cell application. Pt supported on ceria, and Pt supported on titania show a very good low temperature water gas shift activity, and emerges as a promising new generation of non pyrophoric noble metal based catalysts. Literature study show a profound disagreement about the active structure of platinum in these catalysts, while some claim single atom Pt is active [1], others claim small Pt nanoparticles to be active [2]. This debate also expands further regarding the role of alkali metal promotional effect. Some studies correlate the alkali metal promotion to enhanced dispersion and activity of the Pt single atoms [3,4], whereas other studies attribute the promotion effect to increased stability and activity of the Pt nanoparticles [5]. We investigate the supported Pt catalysts under reaction conditions to understand the role of the alkali promotion and the nature of the active site by using ambient pressure photoelectron spectroscopy (APXPS). APXPS shows the electronic nature of both Pt atom and the sodium metal and their evolution during the reaction.

1. Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science,* **2003**, 301, 935–938.
2. W. Damion Williams, Mayank Shekhar, Wen-Sheng Lee, Vincent Kispersky, W. Nicholas Delgass, Fabio H. Ribeiro, Seung Min Kim, Eric A. Stach, Jeffrey T. Miller, Lawrence F. Allard, *J. Am. Chem. Soc.,* **2010**, 132, 14018–14020.
3. Yanping Zhai, Danny Pierre, Rui Si, Weiling Deng, Peter Ferrin, Anand U. Nilekar, Guowen Peng, Jeffrey A. Herron, David C. Bell, Howard Saltsburg, Manos Mavrikakis, Maria Flytzani-Stephanopoulos, *Science,* **2010,** 329, 1633-1636.
4. Ming Yang, Jilei Liu, Sungsik Lee, Branko Zugic, Jun Huang, Lawrence F. Allard, Maria Flytzani-Stephanopoulos, *J. Am. Chem. Soc.,* **2015**, 137, 3470−3473.
5. Jorge H. Pazmiño, Mayank Shekhar , W. Damion Williams , M. Cem Akatay , Jeffrey T. Miller, W. Nicholas Delgass, Fabio H. Ribeiro, *J. Cat.,* **2012**, 286, 279-286.

Mesoionic Iridium Complexes: Comparing CAN and Electrochemical Water Oxidation

M. Olivares[1], M. Li[2], C. Van der Ham[3], S. Bernhard[2], D. Hetterscheid[3], M. Albrecht[1]*

[1]Universität Bern, [2]Carnegie Mellon University, [3]Leiden University

Water oxidation is one of the two half reactions of water splitting and the critical step due to the high potential required to drive the reaction. [1] Iridium-based complexes show remarkably high activity for water oxidation, and homogeneous catalysis has demonstrated in various cases. [2,3] Here we will discuss a new family of iridium(III) complexes containing mesionic ligands. These ligands have been modified selectively (Fig. 1) and the influence of various functional groups on catalytic water oxidation have been investigated, providing a rational approach to increase catalytic activity. A critical comparison of CAN- and electrochemically driven water oxidation will be presented.

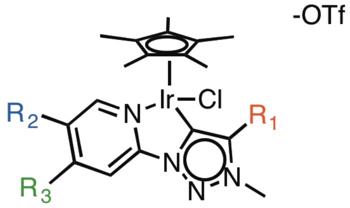


Figure 1. General structure for Ir complexes

[1] Thomsen J. M., Huang D. L., Crabtree R. H., Brudvig G. W.; *Dalton Trans.*, **2015**, *44*, 12452.
[2] Kärkäs M. D., Verho O., Johnston E. V., Åkermark B.; *Chem. Rev.*, **2014**, *114*, 11863.
[3] Woods J. A., Bernhard S., Albrecht M.; *Molecular Water Oxidation Catalysis*, **2014**, John Wiley Sons, Ltd, p. 113.br

Synthesis and Photocatalytic Water Oxidation Study of New Co_4O_4 Cubane Complexes

F. Song[1], G. R. Patzke[1]

[1]Department of Chemistry, University of Zurich

Developing highly active molecular water oxidation catalysts (WOCs) is an important way to overcome the bottleneck of water splitting. $Co_4^{III}O_4$ (with pyridine ligand and modified pyridine ligand) and $Co_4^{II}O_4$ (with 2-(hydroxymethyl)-pyridine ligand) cubanes have been reported as high performance WOCs.[1-3] The 3d-4f Co_3LnO_4 cubanes that possess a bioinspired cubic core were the first heterometallic cubane WOCs.[4] Compared to their homometallic counterparts, such heterometallic cubanes exhibited an improved photocatalytic water oxidation activity. Several new cubane compounds have been synthesized and characterized by single crystal X-ray diffraction, PXRD, FT-IR, UV-Vis and ICP. The photocatalytic water oxidation activities of these new cubanes were studied.

[1] Nicholas McCool, David Robinson, John Sheats, G. Charles Dismukes, *J. Am.Chem. Soc.,* **2011**, 133, 11446-11449.
[2] Serena Berardi, Giuseppina Ganga, Mirco Natali, Irene Bazzan, Fausto Puntoriero, Andrea Sartorel, Franco Scandola, Sebastiano Campagna, Marcella Bonchio, *J. Am. Chem. Soc.,* **2012**, 134, 11104-11107.
[3] Fabio Evangelisti, Robin Güttinger, René Moré, Sandra Luber, Greta Patzke, *J. Am.Chem. Soc.,* **2013**, 135, 18734-18737.
[4] Fabio Evangelisti, René More, Florian Hodel, Sandra Luber, Greta Patzke, *J. Am. Chem. Soc.,* **2015**, 137, 11076-11084.

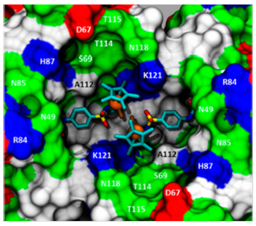
Circularly permutated and chimeric streptavidins as scaffolds for artificial metalloenzymes

M.M. Pellizzoni[1], C. Tinberg[2], D. Baker[2], F. Schwizer[1], T. R. Ward[1]*

[1]University of Basel, [2]University of Washington

Artificial metalloenzymes (ArMs), resulting from the combination of an abiotic cofactor with a host protein, enable the most attractive features of homogeneous and enzymatic catalysis to be merged. Combination of biotinylated metal cofactors with streptavidin variants allows the self assembly of ArMs. The efficiency and selectivity of such systems can be optimized either by chemical modification of the metal moiety or by genetic engineering of the host protein.

The vestibule of the biotin binding site in Streptavidin (Sav) is ideally suited for catalysis (PDB: 3PK2).The remarkable robustness of Sav and the exposure of the cofactor to the medium offers the opportunity to further tailor the active site by introduction of additional structural features.

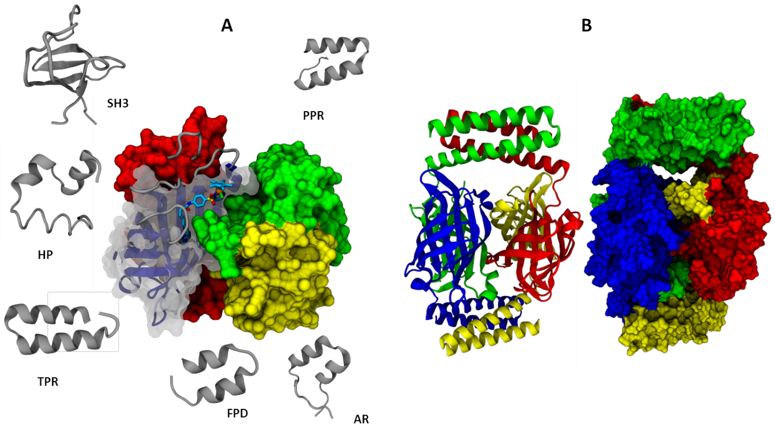


X-ray structure (PDB: 3PK2)

Two strategies were explored: introduction of modified natural motifs (chimeric streptavidin) and computationally designed four helix bundle in circularly permutated Sav.

The introduction of additional structured motifs allow us to explore diverse chemical space around the active site improving the control on the catalytic event thanks to the additional second coordination sphere elements. The newly introduced motifs might form a protective lid over the active site, resulting in ArMs able to perform catalytic reactions in cell free extracts or even *in vivo*.

The new Sav library greatly expands the genetic diversity that has been accumulated in the Ward group in the past decade. The biotin-binding proteins will be combined with biotinylated organometallic cofactors developed in our group to perform e.g. the following bioorthogonal reactions: i) transfer hydrogenation using formate as hydride source, ii) ring-closing metathesis, iii) allylic substitution, iv) C–H activation and v) cyclopropanation.



A. Cartoon representation of well structured and conserved peptide motifs to be engineered in Sav to generate Chimera proteins: **B**. Cartoon and surface representation of a circularly permutated Sav variant (Cp_64/67) bearing a four α-helix bundle on top of the active site.

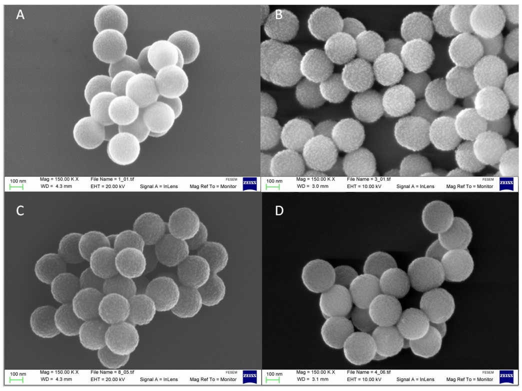
Activity Improvement by Immobilization and Protection of Artificial Imine Reductase on Silica Nanoparticles

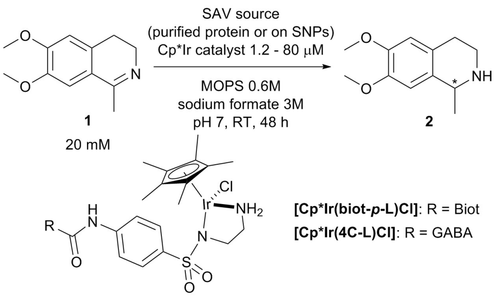
M. Ribar Hestericová[1], R. Correro[2], M. Lenz[3], P. Shahgaldian[2], T. R. Ward[1]*

[1]University of Basel, [2]University of Applied Sciences and Arts Northwestern Switzerland, FHNW, [3]School of Life Sciences, Institute for Ecopreneurship, Muttenz

Artificial metalloenzymes are created by a non-covalent incorporation of an organometallic cofactor within a protein.[1,2] Such system based on the biotin-streptavidin technology combines organometallic and enzymatic catalysis [3,4], and can thus catalyze multiple processes. With the aim of immobilizing Artificial Transfer Hydrogenase (ATHase) on silica nanoparticles (SNPs) and performing NAD+ regeneration in situ, we selected the enantioselective transfer hydrogenation of cyclic imines as a model reaction.

Various streptavidin isoforms were pre-incubated with the biotinylated iridium cofactor and lyophilized to obtain the functional artificial metalloenzymes. These hybrid catalysts were embedded within a protective organosilica layer [5] yielding active SNPs.





Upon immobilization and protection of streptavidin mutants on the SNPs, the resulting nanoparticles display remarkable catalytic activity with TON = 46000 under the applied conditions for the reduction of 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline, with the possibility to recycle the active catalyst. The concentration of the active Cp*Ir catalyst was determined by means of ICP-MS measurements. This protected system is also able to retain its activity in the presence of cellular debris.

[1] Ward, T. R. *Acc. Chem. Res*. **2011***, 44*, 47.
[2]Lu, Y. *Nature* **2009**, *460*, 855.
[3] Dürrenberger, M. *Angew. Chem. Int. Ed*. **2011**, *50*, 3026.
[4] Köhler V. *Nature Chem.* **2013**, *5*, 93.
[5] Cumbo, A. *Nat. Commun.***2013**, 4.

Sol-Gel Processed Multicomposite Nanostructured Hematite-Titania Photoanode with Improved Oxygen Evolution: The Role of the Oxygen Evolution Catalyst

M. Bärtsch[1], R. Solarska[2], M. Sarnowska[2], O. Krysiak[2], J. Augustyński[2]*, M. Niederberger[1]*

[1]ETH Zurich, [2]University of Warsaw

Solar-driven fuel production such as photoelectrochemical water splitting is a direct way to a clean hydrogen source and requires a smaller bias than electrolysis of water.

Among the metal oxides that are possible candidates, hematite is an interesting material due to its relatively narrow band gap of *ca.* 2.1 eV which enables a maximum solar-to-hydrogen efficiency of 15.5%, corresponding to 12.6 mA/cm^2.[1] In practice, the photocurrent is much lower since low e/h mobility, low conductivity and fast exciton recombination limit the photocurrent. Additionally, a large overpotential needs to be applied to achieve reasonable current densities due to poor hole transfer at the surface linked to sluggish oxygen evolution kinetics.

We present an approach that tackles these drawbacks as follows: Through the introduction of heterojunctions, charge carriers are promoted to the surface (holes) or to the back (electrons) in a cascade charge transfer. A liquid phase process was pursued in which the preformed iron oxide and anatase titania nanoparticles were spin coated on an F:SnO_2 (FTO) substrate. The increase in photocurrent thanks to titania incorporation is partially attributed to the formation of an active interface Fe_2TiO_5 that is formed upon annealing, while TiO_2 seems to disappear completely.[1]

In addition, we added a layer of amorphous mixed metal oxide as water oxidation catalyst with the composition $Fe_{20}Cr_{40}Ni_{40}O_x$ by a simple spin coating deposition process.[2] The performance further rose from 2.6 mA/cm^2 to 3.0 mA/cm^2 and the multicomposite photoanode exhibited a durability of at least 24 hrs. During this talk, we provide further insights into the changes that occur after introducing the oxygen evolution layer.

To sum up, our study demonstrates the simplicity of this method leading to photoanodes with comparable performances as CVD processed photoanodes.[3,4] This work paves the way for understanding the mechanism of other dopant and co-catalyst induced changes and could be combined with other materials.

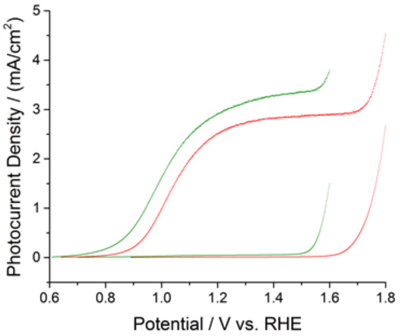


Figure 1 Performance of an unmodified hematite-titania photoanode (shown in red) and after the addition of the amorphous $Fe_{20}Cr_{20}Ni_{20}O_x$ overlayer (shown in green). Conditions: 1M NaOH (pH=13.6), 10 mVs^{-1} scan rate, uncorrected for ohmic losses. The dark currents are shown in the corresponding colors. Photocurrents correspond to AM 1.5 G 100 mWcm^{-2} simulated solar light.

[1] D.Monllor-Satoca, M. Bärtsch, C. Fàbrega, A. Genç, S. Hilaire, T. Andreu, J. Arbiol, M. Niederberger, J. R. Morante, *Energy Environ. Sci.*, **2015**, 8, 3242-3254.

[2] J. B. Gerken, S. E. Shaner, R. C. Massé, N. J. Porubsky and S.S. Stahl,*Energy Environ. Sci.*, **2014**, 7, 2376-2382.

[3] A. Kay, I. Cesar and M. Grätzel, J. Am. Chem. Soc., **2006**, 128 (49), 15714–15721.

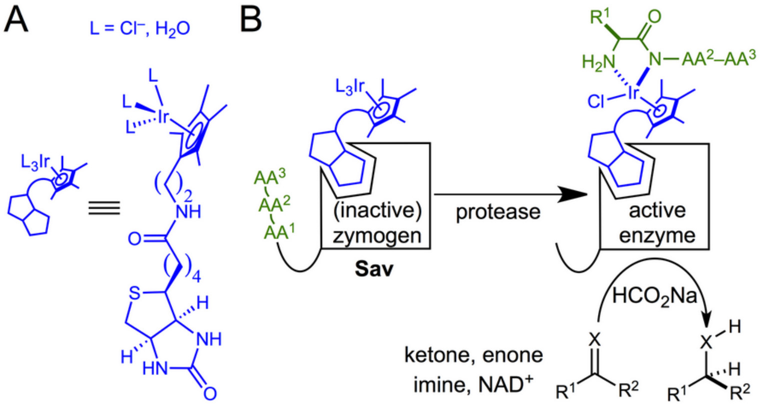
[4] S. D. Tilley, M. Cornuz, K. Sivula, M. Grätzel, *Angew. Chem. Int. Ed.*, **2010**, 49, 6405–6408.

Upregulation of an Artificial Zymogen by Proteolysis

V. Lebrun[1], Z. Liu[1], T. Kitanosono[2], H. Mallin[1], V. Köhler[1], D. Häussinger[1], D. Hilvert[3], S. Kobayashi[2], T. R. Ward[1]*

[1]University of Basel, [2]The University of Tokyo, [3]ETH Zurich

Complex biochemical cascades, which are essential to sustain life, rely on tightly cross-regulated enzymatic processes. Several complementary mechanisms are used by the cell to achieve such exquisite regulation including (i) the control of the expression, (ii) chemical modification, (iii) allosteric regulation and (iv) selective proteolysis by protease.[1] The latter strategy consists in expressing an enzyme in an inactive state, also called zymogens, and activating them via partial proteolysis by a cognate protease. In recent years, artificial metalloenzymes, resulting from anchoring an organometallic catalyst within a macromolecular scaffold, have emerged as an attractive alternative to organometallic catalysts.[2,3] With the aim of developing of biocompatible strategy for the upregulation of an artificial metalloenzyme, we report the development and the genetic optimization of an artificial zymogen requiring the action of a natural protease to unleash its latent asymmetric transfer hydrogenase activity (Figure 1).



[1] J. M. Berg, J. L. Tymoczko, L. Stryer, *Biochemistry, 7th Edition*, W H Freeman, New York, **2012**.
[2] O. Pàmies, M. Diéguez, J.-E. Bäckvall, *Adv. Synth. Catal.* **2015**, *357*, 1567–1586.
[3] T. Heinisch, T. R. Ward, *Eur. J. Inorg. Chem.* **2015**, 3406–3418.

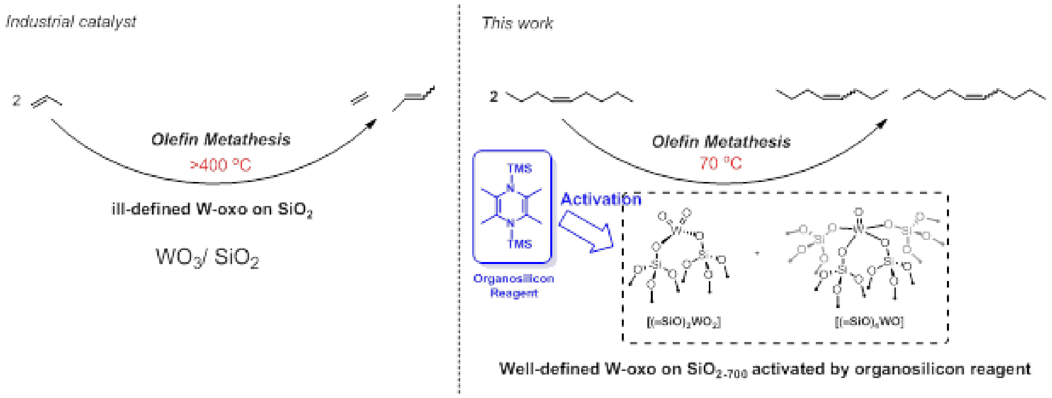
Unprecedented Activity of Silica-supported Tungsten-oxo in Olefin Metathesis

K. W. Chan[1], V. Mougel[1,4], G. Siddiqui[1], K. Kawakita[2], H. Nagae[2], H. Tsurugi[2], O. V. Safonova[3], C. Copéret[1]*, K. Mashima[2]*

[1]ETH Zurich, [2]Osaka University, [3]Paul Scherrer Institute, Villigen, [4]Collège de France

WO_3/SiO_2 is a well-known olefin metathesis catalysts used in industry. However, it requires high temperature (› 400 °C) to achieve significant activity, making its use restricted to unfunctionalized olefins. In addition, the structure and reaction mechanism of this classical catalyst is still unknown.

We have recently developed new synthetic strategies based on surface organometallic chemistry (SOMC) to prepare well-defined silica-supported tungsten-oxo catalyst which shows unprecedented activity in olefin metathesis upon activation by organosilicon reducing agent at low temperature. The structure of the activated catalyst was investigated by IR, UV-Vis, EPR, ss NMR and XAS. In addition, further studies in the interaction of ethylene and the activated catalyst provide insight into the reaction mechanism which shed light on the initiation mechanism of olefin metathesis for the heterogeneous industrial catalyst.



[1] V. Mougel, C. Copéret, K. Mashima, H. Tsurugi, H. Nagae.**Activation of olefin metathesis catalysts by organic reductants.** Publication number: P166256EP. Publication date: pending.

Selective deposition of zinc on copper surface by chemical vapor deposition, a selective catalyst for carbon dioxidehydrogenation

S. Saedy[1], J. Lee[1], M. Ranocchiari[1], J. A. van Bokhoven[2,1]*

[1]Paul Scherrer Institute, Villigen, [2]ETH Zurich

Bimetallic catalysts play very important role in the chemical industry. High interaction of different species is a bottleneck for optimized catalytic performance. The conventional approaches for those catalysts often result in a broad particle size distribution and non-uniform active sites; leading to different competitive reactions which proceed simultaneously on the catalyst surface.[1] In case of bimetallic catalysts, the lack of precise control of chemical composition and structure of nanoparticles on support leads to a non-uniform mixture of monometallic and bimetallic particles. This non-uniform and heterogeneous structure obfuscate linking the catalyst activity to the structure and composition.[2]

Copper-zinc catalyst is a well-known catalyst which is utilized in carbon dioxide hydrogenation to valorize this greenhouse gas. A good interaction between copper and zinc particles and the synergic effect of copper and zinc provide great increments of catalytic activity toward methanol formation. The methanol productivity closely correlates to the number of contact point between copper and zinc atoms.[3]In this work, we present an efficient method of selective gas phase deposition[4]of zinc on the copper surface supported on alumina. The zinc is selectively reacted on the copper particles, which maximizes the interaction between copper and zinc. The catalyst showed high catalytic activity and selectivity on carbon dioxide hydrogenation to methanol compared to a co-precipitated catalyst, confirming enhanced interaction of copper and zinc in the particles (Fig. 1). The structure of the catalysts was determined by scanning tunneling electron microscopy imaging and powder X-ray diffraction. The results confirmed perfect dispersion and interaction of copper-zinc atoms.

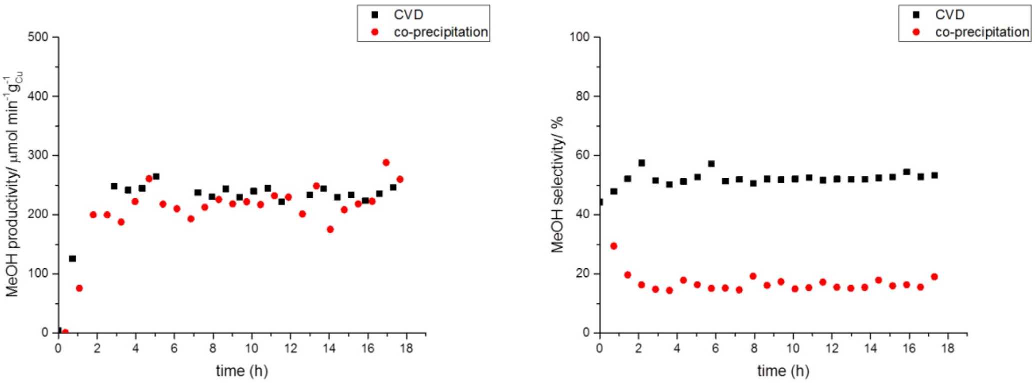


Fig. 1: Methanol productivity and selectivity over CuO-ZnO/Al2O3synthesized via CVD (■) and co-precipitation (●)

[1] O'Neill, B. J.; Jackson, D. H. K.; Lee, J.; Canlas, C.; Stair, P. C.; Marshall, C. L.; Elam, J. W.; Kuech, T. F.; Dumesic, J. A.; Huber, G. W. *ACS Catal.* **2015**, *5*, 1804.
[2] Lu, J.; Low, K.-B.; Lei, Y.; Libera, J. A.; Nicholls, A.; Stair, P. C.; Elam, J. W.*Nat. Commun.* **2014**, *5*.
[3] Tisseraud, C.; Comminges, C.; Belin, T.; Ahouari, H.; Soualah, A.; Pouilloux, Y.; Le Valant, A. *J. Catal.* **2015**, *330*, 533.
[4] Parnian, M. J., Khodadadi, A. A., Taheri Najafabadi, A., Mortazavi, Y.; Appl. Catal., A: Gen. **2014**, 470, 221.b

A Solvent Switchable Catalyst for the Transformation of HMF into Valuable Products

S. Siankevich[1], P. Dyson[1]

[1]EPF Lausanne

In the last few years the production of 1st and 2nd generation biofuels and commodity chemicals from, primarily, lignocellulosic biomass has attracted the attention of the chemical industry. This bio-based production of commodity chemicals is of increasing interest since it results in environmentally friendly processes and products with reduced carbon footprint with the added benefit of making us independent from the petrochemical feedstocks. However, the conversion of biomass into useful chemical intermediates requires novel catalytic systems able to selectively transform key intermediates such as sugars or 5-hydroxymethylfurfural (HMF) into other chemicals under moderate conditions. Herein, we demonstrate a new bimetallic, rhodium-nickel nanocatalyst immobilized inside the core of hollow carbon hollow spheres. The nanocatalyst was evaluated in the hydrogenation of HMF and affords different valuable products as a function of the solvent.

Isothermal stepped conversion of methane to methanol at elevated methane pressures

M. Ranocchiari[1], P. Tomkins[2], J. A. van Bokhoven[2,1]*

[1]Paul Scherrer Institute, Villigen, [2]ETH Zurich

Methane is a promising energy source for the transition towards carbon-free fuels. The low energy density makes transportation costs high. Thus, simple liquefaction of methane to higher value-added chemicals is a desirable process, but challenging to achieve, because of the higher reactivity of methanol than methane. A decade ago, the cyclic conversion of methane to methanol over copper-supported zeolites was discovered.[1] In this process the catalyst is activated in oxygen at high temperature (typically 450 °C) and subsequently reacts with methane at a lower temperature in the absence of any oxygen (Figure 1). Many efforts have been made to improve the catalyst under these conditions, but the big temperature difference between activation and reaction makes the process still comparably tedious. Prior reports mainly explored the catalyst scope and the influence of the temperature on the activation of the catalyst. By using a well-known material for this conversion, namely copper exchanged mordenite (Cu-MOR), but increasing the methane pressure during reaction from the typically used 50 mbar in helium to 36 bar, the yield dramatically increases from 14 $\mu\text{molMeOH}\bullet\text{gcat}^{-1}$ to 103 $\mu\text{molMeOH}\bullet\text{gcat}^{-1}$.[2] Operating the activation and reaction at the same temperature is highly favorable, because this omits the tedious heating procedures and allows for faster cycling. Almost no methanol is extracted, if activation and reaction with 50 mbar methane are carried out at 200 °C. When the reaction is performed at elevated methane pressures up to 37 bar, steadily increasing yields of up 56 $\mu\text{molMeOH}\bullet\text{gcat}^{-1}$ are reached.[2] The obtained yields are much higher than with the old protocol involving high temperature activation and reaction with 50 mbar methane. There is no spectroscopic signature of the classically described µ-oxo-dicopper active site. Thus, the reaction proceeds via a new mechanism, involving copper clusters as the active species. Further, Cu-Y, a material that was described not to be active with the old protocol was active under isothermal conditions at elevated pressure. The herein presented isothermal conversion of methane to methanol at elevated pressures opens new avenues for material synthesis and brings one of the most difficult reactions a bit closer to possible industrial application.

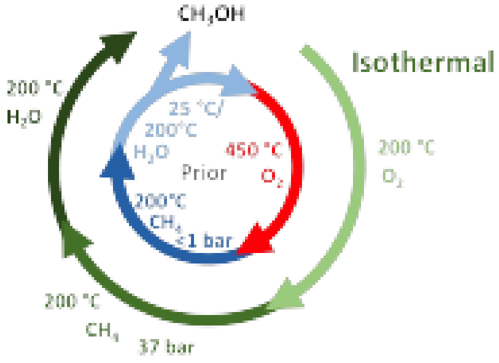


Figure 1. Prior high temperature route and the presented isothermal stepped methane to methanol reaction.

[1] M. H. Groothaert, P. J. Smeets, B. F. Sels, P. A. Jacobs and R. A. Schoonheydt, JACS, 2005, 127, 1394.

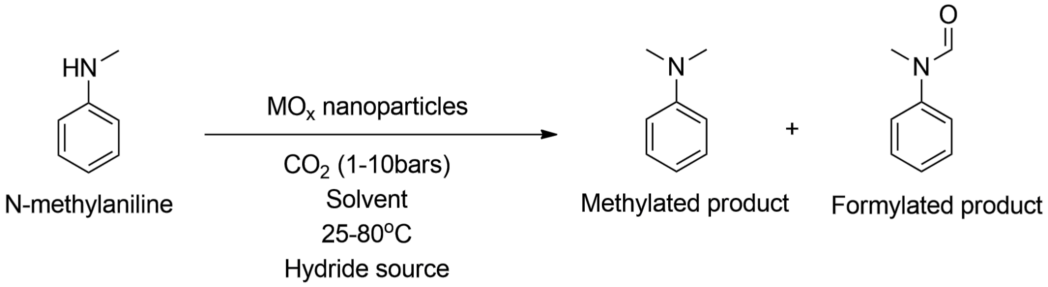
[2] P. Tomkins, A. Mansouri, S. E. Bozbag, F. Krumeich, M. B. Park, E. M. C. Alayon, M. Ranocchiari and J. A. van Bokhoven, Angew. Chem. Int. Ed., 2016, 55, 5467.

Earth abundant metal oxide nanoparticles as recyclable catalysts for N-methylation and N-formylation reactions using CO_2 as the C1 source in mild conditions.

A. Gopakumar[1], P. J. Dyson[1]*

[1]LCOM, EPF Lausanne

CO_2 is an abundant, renewable, cost-effective and green C1 resource [1]. A sustainable way to fix CO_2 with amines through the reductive functionalization of CO_2 to generate the corresponding formylation products as well as methylation products is attractive [2]. Several catalysts have been reported, but all present certain drawbacks [3]. Herein, we report a novel, simple and inexpensive catalytic approach employing earth-abundant metal oxide nanoparticles that operate in a one-pot reaction under mild conditions. N-methylaniline was used as the model substrate to study the effects of catalytic loading, reaction time, temperature, pressure, various hydride sources and solvents. High conversion and chemo-selectivity for the products could be realized. Altogether, the new catalyst offers a green, recyclable, and economically viable way of fixing CO_2 to produce value-added chemicals.



[1] (a) W. Wang, S. P. Wang, X. B. Ma and J. L. Gong, *Chem. Soc. Rev.*, **2011**, 40, 3703; (b) J. F. Shi, Y. J. Jiang, Z. Y. Jiang, X. Y. Wang, X. L. Wang, S. H. Zhang, P. P. Han and C. Yang, *Chem. Soc. Rev.*,**2015**, 44, 5981; (c) Y. W. Li, S. H. Chana and Q. Sun, *Nanoscale*, **2015**, 7, 8663; (d) K. Huang, C.-L. Sun and Z.-J. Shi, *Chem. Soc. Rev.*, **2011**, 40, 2435; (e) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, **2007**, 107, 2365; (f) M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev*., **2014**, 114, 1709.
[2] (a) Z. Rappoport, The Chemistry of Anilines, *Wiley InterScience*, **2007**; (b) X.Cui, Y. Zhang, F.Shi, *Chem. Commun.*, **2014**, 50, 189; (c) O. Jaquet, C. D. Gomes, M. Ephritikhine, T. Cantat, *J. Am. Chem. Soc.*, **2012**, 134(6), 2934; (d) S. Das, F. D. Bobbink, G. Laurenczy, P. J. Dyson, *Angew. Chem. Int. Ed.*, **2014**, 53(47), 1286.
[3] Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nature Commun.*, **2015**, 6, 5933.

Development of sulfur-tolerant ruthenium catalyst for dry biomass derived CO methanation.

D. Kuzmenko[1], M. Nachtegaal[1], T. Schildhauer[1], C. Copéret[2]*

[1]Paul Scherrer Institute, Villigen, [2]ETH Zurich

Production of synthetic natural gas (SNG) from dry biomass can be a sustainable alternative to fossil fuels such as natural gas. SNG production involves gasification of the biomass, gas cleaning to remove catalyst poisons such as H2S, COS and thiophene, followed by the methanation step. To make biomass-derived fuel more competitive, it is very important to improve the efficiency of the gas cleaning step. Apart from energy inefficient low temperature scrubbing, there are two options for high temperature sulfur removal: in case of high temperature gasification, a sorbent for removal of the only remaining sulfur species hydrogen sulfide (H_2S) is sufficient; in case of low temperature gasification, a reactor between the gasifier and methanation reactor is added which converts organic sulfur species (e.g. thiophenes) into H_2S.[1]

In order to further optimize the process, gas cleaning can be integrated with methanation. This could be done by, for example, regenerating a sulfur-poisoned Ru/γ-Al_2O_3 catalyst under oxidative conditions followed by reduction (Fig. 1a). Ru metal is chosen because under the conditions typical of methanation and regeneration, unlike Ni, it does not form stable sulfate species that are difficult to reduce.[2] However, the initial methanation activity of the catalyst is not fully recovered. Based on *in situ* X-ray absorption spectroscopy (XAS), it was proposed that aluminum sulfate is formed during regeneration in O_2 and H_2S is evolved as a result of reduction in H_2, resulting in poisoning of Ru metal even under sulfur-free conditions.[3]

The aim of the present study is to develop a support for Ru nanoparticles that would allow complete regeneration of initial methanation activity and stable activity over multiple regeneration cycles. Catalyst testing results indicate that SiO_2 support (Fig. 1b: TEM image of 3% Ru particles on SiO_2) could be a possible alternative to γ-Al_2O_3. Although both Ru/Al_2O_3 and Ru/SiO_2 lost some of their initial activity, Ru/SiO_2 released more SO_2 during O_2 regenerative step (Fig. 1c: SO_2, m/z=64 MS signal during regeneration step) indicating that less sulfur was carried over to the next cycle. The effect of silica surface modification is currently being investigated.

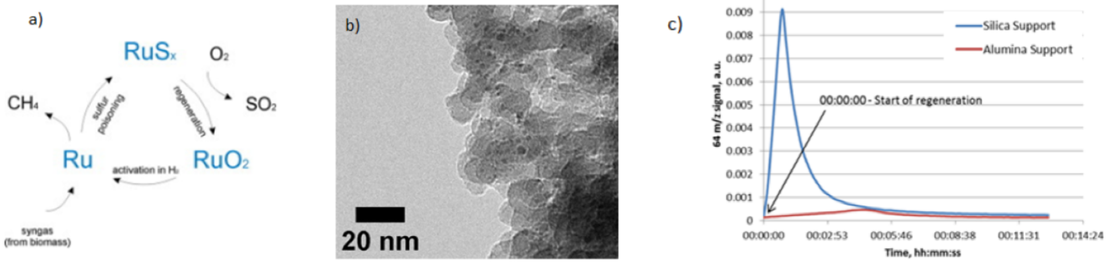


Fig. 1: a) Regeneration cycle, b) TEM image of 3% Ru/SiO_2, c) SO_2 MS signal during regeneration step.

1. J. Kopyscinski et al., *Fuel*, **2010,** 89, 1763–1783.
2. C. F. J. König et al., *Journal of Catalysis*, **2013**, 305, 92 – 100.
3. C. F. J. König et al., *Catalysis Today*, **2014**, 229, 56 – 63.

CHIMIA

CHIMIA 2016, Volume 70
ISSN 0009-4293
www. chimia.ch

SCS
Swiss Chemical
Society

Supplementa to Issue 7-8/2016

SCS Fall Meeting 2016

Oral Presentation Abstracts Session of Catalysis Science & Engineering

September 15, 2016
University of Zurich, Irchel Campus
http://scg.ch/fallmeeting/2016

Swiss Chemical Society
Haus der Akademien
Postfach
3001 Bern
Switzerland
info@scg.ch
www.scg.ch

In situ Studies on the Behavior of Metal/Oxide Catalysts during the Water-gas Shift Reaction

J. A. Rodriguez[1]

[1]Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA

In this talk, it will be shown how a series of *in-situ* techniques {X-ray diffraction (XRD), pair-distribution-function analysis (PDF), X-ray absorption spectroscopy (XAS), environmental scanning tunneling microscopy (ESTM), infrared spectroscopy (IR), ambient-pressure X-ray photoelectron spectroscopy (AP-XPS)} can be combined to perform detailed studies of the structural, electronic and chemical properties of metal/oxide catalysts used for the production of hydrogen through the water-gas shift reaction (WGS, $CO + H_2O \rightarrow H_2 + CO_2$) [1-4]. Under reaction conditions most WGS catalysts undergo chemical transformations that drastically modify their composition with respect to that obtained during the synthesis process [1,2]. The active phase of catalysts which combine Cu, Au or Pt with oxides such as ZnO, CeO_2, TiO_2, CeO_x/TiO_2 and Fe_2O_3 essentially involves nanoparticles of the reduced noble metals. The oxide support undergoes partial reduction and is not a simple spectator, facilitating the dissociation of water and in some cases modifying the chemical properties of the supported metal. Therefore, to optimize the performance of these catalysts one must take into consideration the properties of the metal and oxide phases. IR and AP-XPS have been used to study the reaction mechanism for the WGS on the metal/oxide catalysts [3,4]. Data of IR spectroscopy indicate that formate species are not necessarily involved in the main reaction path for the water-gas shift on Cu-, Au- and Pt-based catalysts. Thus, a pure redox mechanism or associative mechanisms that involve either carbonate-like (CO_3, HCO_3) or carboxyl (HOCO) species should be considered. In the last two decades, there have been tremendous advances in our ability to study catalytic materials under reaction conditions and we are moving towards the major goal of fully understanding how the active sites for the production of hydrogen through the WGS actually work.

[1] J.A. Rodriguez et al, *Catal. Today*, **2009**, *145*, 188-194.
[2] J.A. Rodriguez e al, *Phys. Chem. Chem. Phys.* **2013**, *15*, 12004-12025
[3] K. Mudiyanselage et al, *Angew. Chem.* Int. Ed. **2013**, *52*, 5101-5105
[4] J. Carrasco et al, *Angew. Chem. Int. ed.* **2015**, *54*, 3917-3921

Parahydrogen-based hypersensitive NMR/MRI toolkit for catalysis

I. V. Koptyug[1], K. V. Kovtunov[1], V. V. Zhivonitko[1]

[1]International Tomography Center SB RAS, Novosibirsk, Russia

When parahydrogen is used in catalytic hydrogenations instead of normal H_2, the NMR signals of reaction products and intermediates can be enhanced by 10000-fold and more, owing to the phenomenon of parahydrogen-induced polarization (PHIP). This can clearly facilitate the detection of reaction products and short-lived intermediates not detectable by conventional NMR. Previously, this major advantage has been explored in the context of H_2 activation by transition metal complexes and clusters in solution. Many such catalysts activate H_2 via the formation of metal dihydrides, which is key to PHIP observation as the latter requires incorporation of both H atoms of an H_2 molecule into the same reaction intermediate or product.

To extend PHIP studies from homogeneous to heterogeneous catalysis, it was thus essential to retain the proper H_2 activation mechanism for the hydrogenation reaction. Initially, this was achieved by immobilizing a suitable transition metal complex on a solid support. Our recent results show that several immobilized Rh and Ir complexes can produce PHIP effects both in liquid phase and in gas phase hydrogenations of alkenes and alkynes. Further extension to other types of single-site and/or molecularly defined heterogeneous hydrogenation catalysts is not only possible, but is also highly desirable, and is currently in progress.

In contrast, for supported metal catalysts (e.g., Pt/Al_2O_3) the Horiuti-Polanyi hydrogenation mechanism is intrinsically non-pairwise, and no PHIP effects were expected. Despite that, they were successfully observed both in liquid-solid and in gas-solid heterogeneous hydrogenations of unsaturated substrates catalyzed by various supported metal catalysts as well as several metal oxides and bulk unsupported metals. Thus, PHIP effects are quite common in heterogeneous hydrogenations, providing a remarkable possibility to develop a hypersensitive NMR-based tool for catalytic research. Indeed, the unique chemical specificity of NMR spectroscopy and the non-invasive nature of MRI, combined with the major signal enhancement provided by PHIP, can give access to new knowledge about the mechanisms of important chemical reactions and the dynamic processes in operating reactors. Examples include the application of PHIP to the mechanistic and kinetic studies of heterogeneous hydrogenations of various unsaturated compounds, and MRI of operating gas-solid catalytic reactors. Another promising direction of research is the extension of PHIP to reactions other than hydrogenation of double and triple C-C bonds, as exemplified by the PHIP study of the catalytic oligomerization of unsaturated hydrocarbons and hydrofesulfurization of thiophene. Applications of PHIP to homogeneous catalytic processes are far from being exhausted either. Metal-free catalysts such as frustrated Lewis pairs (FLP) are considered as alternative catalysts for cheaper and greener industrial catalytic hydrogenations. Observation of PHIP effects upon parahydrogen activation by FLP provides a novel powerful instrument for the detailed mechanistic studies of their functioning. Finally, the interest to this field of research extends far beyond catalysis alone, as catalytic PHIP-based enhancement can be extremely useful for providing signal enhancement in various practical applications of NMR and MRI, including biomedical studies of metabolism in vivo.

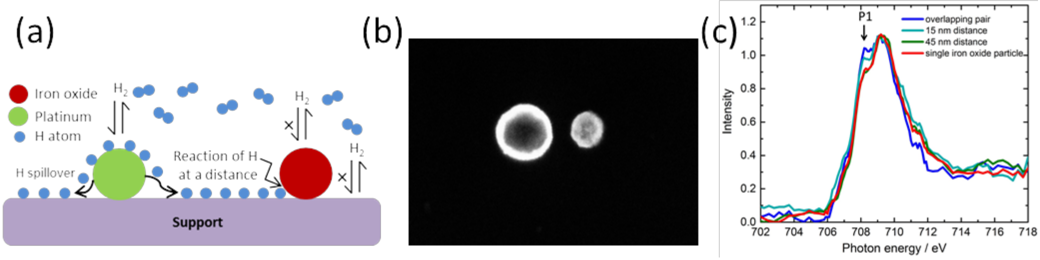
[1] K.V. Kovtunov, O.G. Salnikov, V.V. Zhivonitko, I.V. Skovpin, V.I. Bukhtiyarov, I.V. Koptyug. Catalysis and Nuclear Magnetic Resonance Signal Enhancement with Parahydrogen. *Topics in Catalysis*, **2016** (accepted, in press).
[2] K.V. Kovtunov, V.V. Zhivonitko, I.V. Skovpin, D.A. Barskiy, I.V. Koptyug. Parahydrogen-induced polarization in heterogeneous catalytic processes, Top. Curr. Chem. **2013**, *338*, 123.

A closure to the controversy around hydrogen spillover: a nanolithography and single nanoparticle spectro-microscopy approach

W. Karim[1,2], C. Spreafico[1], A. Kleibert[2], J. Gobrecht[2], J. VandeVondele[1], Y. Ekinci[2], J. A. van Bokhoven[1,2]*

[1]ETH Zurich, [2]Paul Scherrer Institute, Villigen

We employ enhanced precision of top-down nanofabrication [1, 2] and single-particle *in-situ* X-ray absorption spectromicroscopy [2] to visualize hydrogen spillover, which is a critical phenomenon in heterogeneous catalysis [3]. Depending on the nature of the support, hydrogen spillover may occur in hydrogen catalysed reactions, which involve dissociative chemisorption of hydrogen onto a catalytic metal particle followed by migration of hydrogen atoms over the support. This eventually leads to the reaction of the hydrogen atoms with a species away from the hydrogen-splitting catalyst (Fig. 1a). Evidence of the occurrence of hydrogen spillover on non-reducible supports such as alumina is disputed, but has often been assumed to explain catalytic phenomena, while its occurrence on a reducible support like titania is generally accepted. Direct experimental proof of its existence does not exist due the lack of well-defined model systems and the inability to observe the effect directly.



We develop novel model surfaces using extreme ultraviolet (EUV) lithography [1] and electron beam lithography (EBL) [2, 4] to achieve nanometer precision over particle size and its positioning. X-ray photoemission electron microscope (X-PEEM) at the Swiss Light Source (SLS) enables in-situ spectromicroscopy on individual iron particles prepared with nanofabrication [2, 4]. Fifteen pairs of nano-sized iron oxide and platinum particles at varying distances from each other starting at 0 nm to 45 nm are positioned on the same support with an accuracy of one nanometer, previously not achievable. The SEM image in Fig. 1b shows one of the pairs with a 25 nm distance. All pairs along with an iron oxide particle without any platinum in its proximity are probed simultaneously to visualize chemical reduction by hydrogen spillover. The spectra showed that hydrogen spillover on non-reducible alumina support depends on the distance from the catalyst and is relevant only at distances below 15 nm (Fig. 1c), occurring only on special sites. Maximum reduction occurs in the iron oxide particle overlapping with platinum, indicated by the highest intensity in the Fe L2,3 edge spectrum (P1 in Fig. 1c). As the distance from platinum increases, less reduction takes place and the pairs at higher distances, along with the iron oxide particle without platinum in its vicinity, have coinciding spectra which implies no spillover. Spillover on reducible titania support, which occurs via coupled electron-proton transfer, is uniform all over the support irrespective of distance. For the first time, distance dependence of hydrogen spillover has been experimentally visualized, and the hydrogen diffusion and migration mechanisms are elucidated by DFT calculations.

References: [1] W. Karim, S. A. Tschupp, M. Oezaslan, T. J. Schmidt, J. Gobrecht, J. A. van Bokhoven, and Y. Ekinci, *Nanoscale* **7**, 7386 (2015); [2] W. Karim, A. Kleibert, U. Hartfelder, A. Balan, J. Gobrecht, J. A. van Bokhoven, and Y. Ekinci, *Scientific Reports* **6**, 18818 (2016); [3] R. Prins,*Chemical Reviews* **112**, 2714 (2012); [4] W. Karim, S. Clelia, A. Kleibert, J. Gobrecht, J. VandeVondele, Y. Ekinci, and J. A. van Bokhoven, The mechanism of hydrogen spillover in heterogeneous catalysis: seeing is believing, *Manuscript submitted to Nature*(2016).

Photoelectrochemical Water Splitting from Earth-Abundant CuO Thin Film Photocathode: Enhancing Performance and Photo-stability through Deposition of Overlayers

W. Septina[1], R. R. Prabhakar[1], T. Moehl[1], D. Tilley[1], D. Tiley[1]*

[1]Department of Chemistry, University of Zurich

Cupric oxide (CuO) is a promising absorber material for the fabrication of scalable, low cost solar energy conversion devices, due to the high abundance and low toxicity of copper. It is a p-type semiconductor with a band gap of around 1.5 eV, absorbing a significant portion of the solar spectrum. One of the main challenges in using CuO as solar absorber in an aqueous system is its tendency towards photocorrosion, generating Cu_2O and metallic Cu. Although there have been several reports of CuO as a photocathode for hydrogen production, it is unclear how much of the observed current actually corresponds to H_2 evolution, as the inevitability of photocorrosion is usually not addressed.

In this research, we investigated the effect of the deposition of overlayers onto CuO thin films for the purpose of enhancing its photostability as well as performance for water splitting applications. CuO thin film was fabricated by galvanic electrodeposition of metallic copper onto gold-coated FTO substrates, followed by annealing in air at 600 ^{o}C. Photoelectrochemical measurement of the bare CuO film using 0.5 M Na_2SO_4 / 0.1 M K_2HPO_4 (pH 5) under simulated AM 1.5 sunlight showed a current density of *ca.* 1.5 mA cm^{-2} (at 0.4 V_{RHE}), which photocorroded to Cu metal upon prolonged illumination. This photocorrosion could be suppressed by deposition of 50 nm-thick TiO_2, deposited by atomic layer deposition. In addition, we found that insertion of an n-type CdS layer, deposited by chemical bath deposition, between the CuO and TiO_2 layers was able to enhance significantly the photocurrent compared to without the CdS layer. A maximum photocurrent of 1.7 mA cm^{-2} (at 0 V_{RHE}) and relatively positive onset potential (*ca.* 0.9 V_{RHE}) was observed using the photocathode stack FTO/Au/CuO/CdS/TiO_2/Pt. Structural, electrochemical, and photostability characterizations of the photocathode as well as results on various overlayers will be presented.

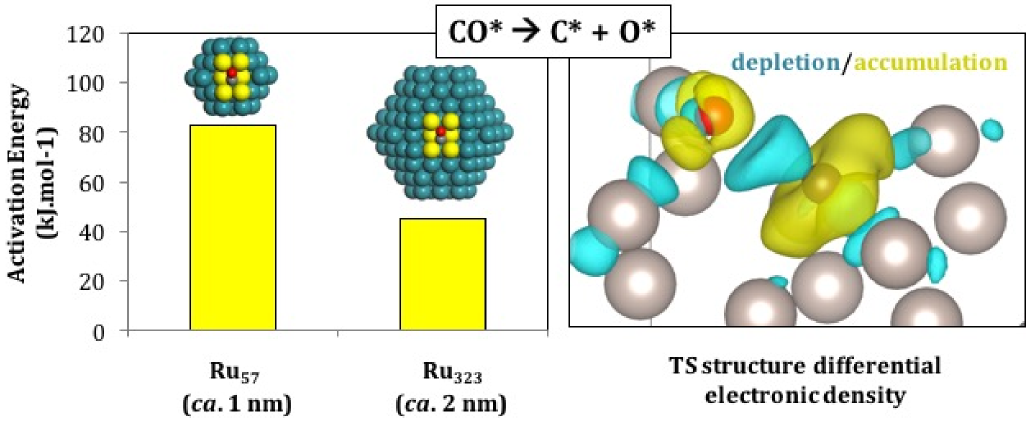
Why Size Matters and Favors CO Activation on Larger Ru Nanoparticles: A Molecular Understanding from First Principles

L. Foppa[1], A. Comas-Vives[1], C. Copéret[1]*

[1]ETH Zurich, Laboratory of Inorganic Chemistry, Vladimir-Prelog-Weg 1-5/10, 8093 Zürich, Switzerland

The activation of the strong CO bond during Fischer-Tropsch Synthesis has long been ascribed to special step-edge sites present on the surface of metal nanoparticle catalysts.[1-3] Accordingly, CO activation rate has been correlated with the abundance of such metal ensembles, which is supposedly low on small clusters (smaller than 5 nm).[4]

In this contribution, by using *ab initio* density functional theory (DFT) calculations on Ruthenium (Ru) nanoparticle models of realistic sizes (1-2 nm) to we evaluate the direct CO activation over a collection of step-edge metal sites on different coordination environments. According to our calculations, C-O bond cleavage is easier over more saturated step-edge Ru sites. We ascribe this effect to the saturation-dependent nature of electron back donation from the metal to the hybrid CO-metal π-symmetry bands on η^2–bound transition-state structures for CO dissociation. We also show that some of the step-edge sites can activate CO with affordable energy barriers even at high coverage conditions under real catalytic conditions.



These findings provide a molecular understanding on the cleavage of strong bonds by step-edge sites, which are believed to be the active sites for several relevant chemical transformations involving CO, NO and N_2. The approach presented here goes beyond the ideal slab models typically used on computational heterogeneous catalysis by exploring the reactivity of metal nanoparticle with realistic size and shapes and by evaluating the substrate-metal bonding contributions to understand the bond activation process with DFT calculations.

[1] Zubkov, T.; Morgan Jr, G. A.; Yates Jr, J. T.; Kühlert, O.; Lisowski, M.; Schillinger, R.; Fick, D.; Jänsch, H. J. *Surface Science* **2003**, *526*, 57.
[2] Tison, Y.; Nielsen, K.; Mowbray, D. J.; Bech, L.; Holse, C.; Calle-Vallejo, F.; Andersen, K.; Mortensen, J. J.; Jacobsen, K. W.; Nielsen, J. H. *The Journal of Physical Chemistry C* **2012**, *116*, 14350.
[3] Shetty, S.; Jansen, A. P. J.; van Santen, R. A. *Journal of the American Chemical Society* **2009**, *131*, 12874.
[4] van Helden, P.; Ciobîcă, I. M.; Coetzer, R. L. J. *Catalysis Today* **2016**, *261*, 48.

Modelling the Phosphorous Dynamics of Vanadyl Pyrophosphate Catalysts

G. Mestl[1], S. Böcklein[1], D. Lesser[1], T. Turek[2]

[1]Clariant Produkte (Deutschland) GmbH, Waldheimerstr. 13, 83052 Heufeld, Deutschland, [2] Institut für Chemische Verfahrenstechnik, TU Clausthal, Leibnizstr. 17, 38678 Clausthal-Zellerfeld, Deutschland

Maleic anhydride (MA) is an important intermediate in chemical industry. It is produced by heterogeneous catalytic oxidation of n-butane in air. Mainly tubular fixed bed reactors are used for this strong exothermal reaction. The catalyst consists of vanadium phosphorous oxides (VPO) and is employed as pelletized full-body shapes. Even after many years of investigation, reaction mechanism and nature of the active sites are not fully understood. An important subject is the slow loss of phosphorous shifting conversion and MA-selectivity in commercially unattractive regions. In order to prevent this phosphorous loss, it is industrial practice adding several ppm of an organic phosphorous compound together with water to the reactor feed [1]. Dynamic experiments in an industrial-scale pilot reactor showed various partially opposed effects on different time scales. From these experiments a kinetic model was derived that accounts for any observed interactions between TMP and water on the VPO surface. The kinetic model was integrated in a two-dimensional, heterogeneous reactor model (gPROMS) which could be successfully applied describing well the temperature profiles and product compositions up to 500 h time on stream.

[1] J. R. Ebner, Monsanto, WO1993016027A1 (1993)

On purpose CO production via methane oxychlorination over heterogeneous catalysts

V. Paunovic[1], G. Zichittella[1], A.P. Amrute[1], J. Pérez-Ramírez[1]*

[1]ETH Zurich

Selective oxidation of methane into carbon monoxide is an appealing approach to valorise the emerging vast natural-gas reserves, as the latter is a key intermediate in the manufacture of commodities such as alcohols, acids, isocyanates, and esters (Fig. 1a).[1] Particularly, this process could be advantageously coupled to the well-established CO conversion into formic acid and/or methanol, which are highly attractive energy carriers.[2] In the present study, we developed a continuous gas-phase catalytic process for the highly selective transformation of CH_4 into CO (Fig. 1a). Therein, CH_4 is reacted with oxygen in the presence of hydrogen chloride over a catalysts enabling the C-H bond functionalization to proceed *via* oxychlorination chemistry, which ischaracterized by significantly lower energy barrier compared to direct oxidation. Chloromethanes ($CH_{4-n}Cl_n$) formed in the latter reaction are oxidized *in situ* on the catalyst surface to produce CO, regenerating HCl, which effectively acts as a reaction mediator (Fig. 1a). In order to identify a mild-oxidizing catalyst, the redox propensity of which can be further controlled by the surface chlorination, a systematic evaluation of different catalyst families was conducted. Vanadium phosphate (VPO) and titanium oxide (TiO_2) appeared to be the optimal catalysts for this process, resulting in exceptionally high CO yields of 30 and 34% at 97 and 90% selectivity, respectively (Fig. 1b). A remarkable CO conversion was only possible when HCl was present in the feed (Fig. 1b), demonstrating its pivotal role in the activation of methane.

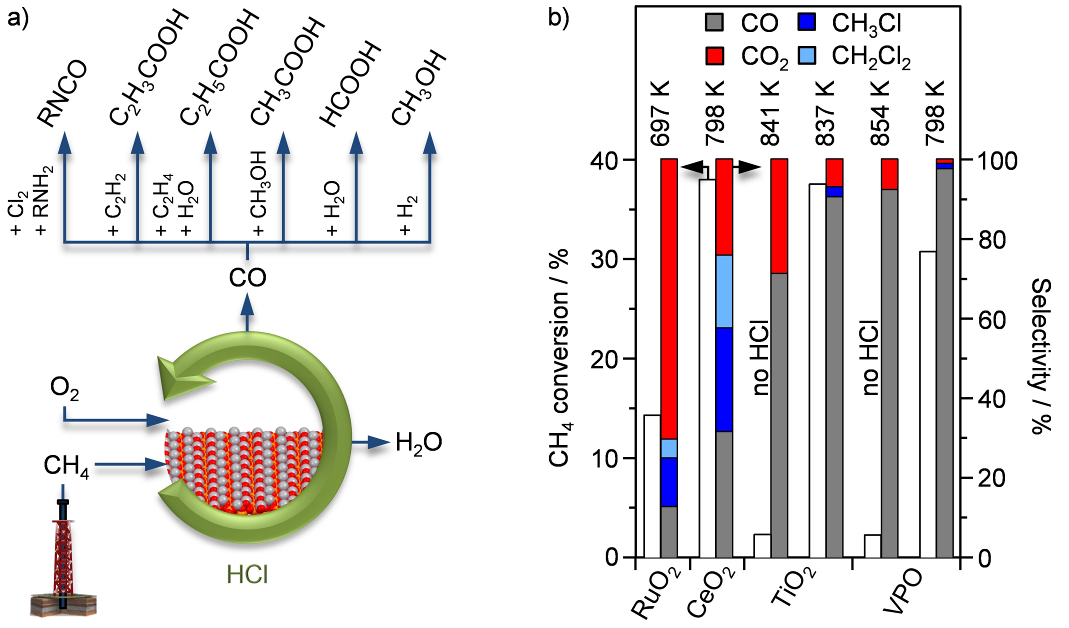


Figure 1 a) Natural gas valorization *via* HCl-mediated selective conversion of CH_4 into CO. b) Performance of different catalysts.

1. J. Bierhals, *Ullman's Encyclopedia of Industrial Chemistry* Vol. 6, 679-693 (Wiley-VCH, Weinheim, 2012).
2. D. Mellmann, P. Sponholz, H. Junge, M. Beller, *Chem. Soc. Rev.* **2016**doi: 10.1039/C5CS00618J.

Rational design of ceria-based supported noble metal catalysts for low temperature CO oxidation using transient X-ray absorption spectroscopy.

R. Kopelent[1], J. A. van Bokhoven[2], M. Nachtegaal[1], M. Bodnarchuk[3], M. V. Kovalenko[3], O. V. Safonova[1]*

[1]Paul Scherrer Institute, Villigen, [2]ETH Zurich/PSI Villigen, [3]ETH Zurich

Rational design of more powerful catalysts requires identification of active intermediates and determination of the structure of active sites. However, this is difficult especially for heterogeneous catalysts because of a large structural heterogeneity of catalytic surfaces. Ceria (CeO_2) is a well-known oxygen storage material which is often used as a support for noble metal catalysts to improve their activity for water-gas-shift reaction, CO oxidation, and three-way catalysis. During low temperature CO oxidation on ceria supported platinum nanoparticles, the reaction most probably occurs at the Pt-CeO_2 interface where CO is provided by platinum and reactive oxygen is provided by ceria[1]. Using state-of-the-art X-ray spectroscopic methods, we recently showed that the reduction of Ce^{4+} to Ce^{3+} is involved in the catalytic cycle of CO oxidation and is part of the rate determining step[2]. Furthermore, we could distinguish between a short-lived active Ce^{3+} species and a longer-lived Ce^{3+} spectator species.

Based on this knowledge, we started a rational design of more active catalysts by introducing dopants (Zr, Nd, Co, Sn, Ti, Bi) into the ceria structure in order to accelerate the reduction step of active cerium atoms. The best homogeneous solid solutions were obtained using Zr or Sn as dopants which was confirmed with XRD and EDX analyses. Platinum nanoparticles of 1.9 nm size with a narrow size distribution were deposited on the surface using a uniform colloidal solution[1]. The narrow size distribution of the platinum nanoparticles was important for comparing the activity of the catalysts normalized to the number of active Pt atoms at the metal-support interface.

As expected, both Sn and Zr dopants significantly increase the reducibility and oxygen storage capacity of ceria, however, only Sn improves the activity of the catalyst for low temperature CO oxidation. To understand this phenomenon, we used transient X-ray absorption spectroscopy at the Ce L_3-edge. We correlated the overall rate of carbon dioxide formation to the rates of Ce^{3+} oxidation and Ce^{4+} reduction during fast switching between CO+O_2 and CO atmospheres. Moreover, we analyzed the reactivity of tin under the same conditions at the Sn K-edge. The identification of true catalytic intermediates and the active sites with transient X-ray absorption and emission techniques will be discussed. The influence of dopants on the catalytic activity of ceria-based supported metal catalysts will be explained.

Acknowledgment: This work was supported by the Swiss National Science Foundation (project number 200021_140750)

[1] Cargnello, M. et al. *Science,* **2013,** 341**,** 771–773.
[2] Kopelent, R. et al. *Angew. Chem. Int. Ed.,* **2015**, 54**,** 8728–8731.

TiO_2 nanocontainers and nanospheres as photocatalysts for CO_2 reduction and photoelectrochemical water splitting: Structural modification.

N. Hérault[1], V. Kaliginedi[2], P. Broekmann[2], K. M. Fromm[1]*

[1]University of Fribourg, [2]University of Bern

CO_2 gas is one of the major factors of the climate imbalance. The reduction of CO_2 by photocatalysis is proposed to convert CO_2 gas into more valuable molecules (such as CH_4, CH_3OH etc.) because solar energy, being an alternative, cheap and environmentally friendly source of energy, can be used as power supply[1]. For this process, titanium dioxide-based materials with various structures are commonly used as photocatalysts[2,3]. Furthermore, the photocatalytic water splitting using the TiO_2-based materials could be a great option for hydrogen production to obtain clean and renewable energy sources[4].

In this project, the TiO_2 nanocontainers and nanospheres (Figure 1 (A), (B)) with different crystalline structures are investigated because the crystalline phase, the size and the shape of TiO_2 may have an influence on its band gap energy and consequently on its photocatalytic properties[5]. Moreover the embedment of silver nanoparticles into the TiO_2 material is explored. Indeed, the presence of silver islands may enhance its photoactivity[6].

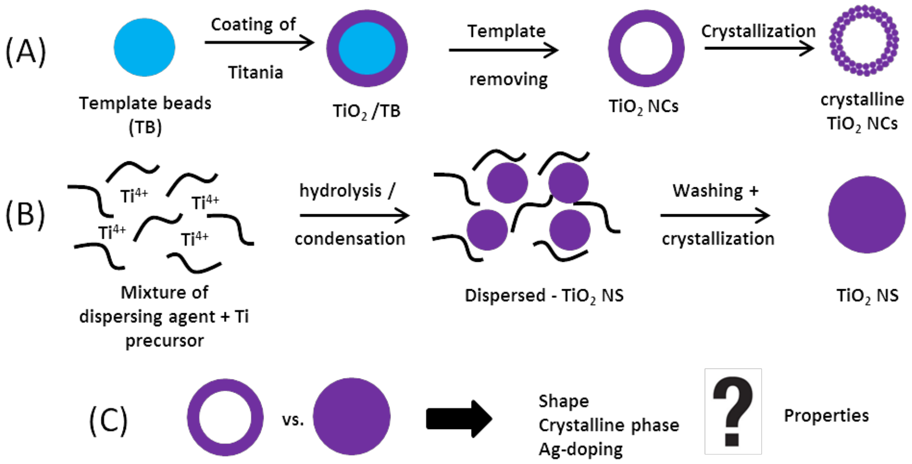


Figure 1: Synthesis of (A) TiO_2 nanocontainers, (B) TiO_2 nanospheres and (C) the study objectives

The objective of this study (Figure 1 (C)) is the correlation between the morphology of the TiO_2-based materials and their photocatalytic properties for the CO_2 reduction and the photoelectrochemical water splitting.

[1] W-N. Wang, J. Soulis, Y. J. Yang, P. Biswas, *Aerosol Air Qual. Res*. 14, 533-549 (2014)
[2] T. Wang, X. Meng, P. Li, S. Ouyang, K. Chang, G. Liu, Z. Mei, J. Ye, *Nano Energy*. 9, 50–60 (2014)
[3] P-Q. Wang, Y. Bai, J-Y. Liu, Z. Fan, Y-Q. Hu, *Catal. Commun*. 29, 185–188 (2012)
[4] M. Ni, M.K.H. Leung, D.Y.C. Leung, K. Sumathy, *Renew. Sustainable Energy Rev*. 11, 401–425 (2007)
[5] Y. Ma, X. Wang, Y. Jia, X. Chen, H. Han, C. Li, *Chem. Rev*. 114, 9987−10043 (2014)
[6] D. Kong, J. Ziang Yie Tan, F. Yang, J. Zeng, X. Zhang, *Appl. Surf. Sci*. 277, 105–110 (2013)

Understanding of the role of Fe in highly active and stable Ni-Fe dry reforming catalysts

S. Kim[1], P. M. Abdala[1], T. Margossian[1], L. Foppa[1], A. Comas-Vives[1], D. Hossein[1], A. Armutlulu[1], C. Müller[1]*, C. Copéret[1]*

[1]ETH Zurich

One major drawback of Ni-based dry reforming ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$) catalysts is the rapid deposition of coke, leading to catalyst deactivation.[1,2] Recently, the alloying of Ni with transition metals has been proposed as a concept to decrease the coking tendency of Ni, albeit often contradictory results have been obtained. To this end, Ni-Fe catalysts embedded in a thermally stable $Mg_xAl_yO_z$ matrix have been developed. The formation of alloyed Ni-Fe nanoparticles was confirmed via TEM-EDX, XRD and XAS measurements. The catalytic performance of monometallic Ni and Fe as well as the bimetallic catalysts was evaluated at 650 °C. Bi-metallic catalysts, in particular, Ni_4Fe_1 (2.6 h^{-1} of TOF_{CH4}) showed a high activity and stability when compared to monometallic Ni (1.8 h^{-1} of TOF_{CH4}) and Fe (0.4 h^{-1} of TOF_{CH4}) catalysts that showed a fast deactivation and a low catalytic activity, respectively. *In situ* XAS measurement revealed the formation of FeO in bimetallic Ni-Fe under DRM conditions, whereas Ni was maintained in its metallic state, Ni^0, both for Ni and Ni-Fe catalysts. The formation of a layer of FeO on an Ni-enriched Ni-Fe alloy was confirmed by probing the diffusion dynamics of Ni-Fe films and DFT calculations. Furthermore, using combined in-situ XAS and XRD experiments, we could demonstrate that FeO removes carbon deposited via a redox mechanism (C + FeO → CO + Fe).

[1] V.C.H. Kroll, H.M. Swaan, S. Lacombe, C. Mirodatos, *J. Catal.*,**1996**, 2, 387-398
[2] E. Ruckenstein and Y.H. Hu, *J. Catal.*,**1996**, 2, 230-238
[3] S. A. Theofanidis, V. V. Galvita, H. Poelman, G. B. Marin, *ACS Catal.*, **2015**, 5, 3028-3039

Chemical layer deposition of porous alumina overcoats increases activity and stability in liquid phase catalytic conversion of biomass-derived chemicals

F. Héroguel[1], B. le Monnier[1], J. Luterbacher[1]*

[1]EPF Lausanne

Biomass-derived chemicals represent an attractive sustainable alternative to petrochemicals. However, the competitiveness of these processes has been limited by the low stability of metal catalysts under the severe conditions used during biomass upgrading.[1] In order to prevent metal leaching and sintering, we developed a chemical layer deposition (CLD) overcoating technique based on the control over aluminum alkoxide surface reactions kinetics and stoichiometry. After deposition of 30 cycles of an alumina overcoat onto alumina supported copper nanoparticles, imaging using high angle annular dark field scanning transmission electron microscopy (HAADF STEM) revealed a conformal porous overcoat. This porosity was was characterized and quantified by nitrogen physisorption. The overcoat suppressed irreversible catalyst deactivation during the liquid-phase hydrogenation of furfural. While a significant loss of activity due to mass transfer limitations and metal coverage by the overcoat was observed by O’Neill *et al.* when using atomic layer deposition (ALD),[2] most of the surface metal sites remained accessible with CLD as confirmed by chemisorption, illustrating the benefits of overcoats porosity that can be targeted by tuning synthesis parameters. Current work is focused on tuning this porosity for the synthesis of shape selective catalyst overcoats.

[1] Florent Héroguel, Bartosz Rozmysłowicz, Jeremy S. Luterbacher, *Chim. Int. J. Chem.,* **2015**, 10, 582-591.
[2] Brandon J. O’Neill, David H. K. Jackson, Anthony J. Crisci, Carrie A. Farberow, Fengyuan Shi, Ana C. Alba-Rubio, Junling Lu, Paul J. Dietrich, Xiangkui Gu, Christopher L. Marshall, Peter C. Stair, Jeffrey W. Elam, Jeffrey T. Miller, Fabio H. Ribeiro, Paul M. Voyles, Jeffrey Greeley, Manos Mavrikakis, Susannah L. Scott, Thomas F. Kuech, James A. Dumesic, *Angew. Chem.,* **2013**, 51, 14053–14057.