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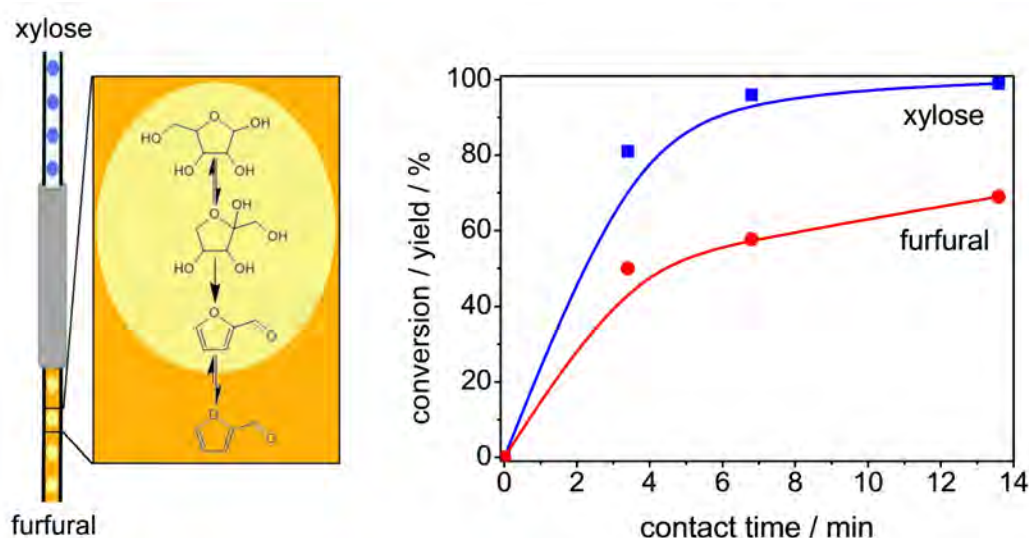
September 11, 2014  
University of Zurich, Irchel Campus  
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## Efficient biphasic processing of sugars to furans over GaUSY/Amberlyst-36 in continuous mode

Christof Aellig<sup>1</sup>, David Scholz<sup>1</sup>, Pierre Dapsens<sup>1</sup>, Cecilia Mondelli<sup>1</sup>, Javier Pérez-Ramírez<sup>1</sup> \*

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Furfural and 5-(hydroxymethyl)furfural have been identified as the most promising intermediates in a future biobased value chain for the production of fuels and chemicals. Both compounds can be obtained through the acid-catalysed isomerization-dehydration of (hemi)cellulose-derived carbohydrates. However, low selectivity is observed in water due to multiple side and consecutive reactions. The use of a biphasic system has been shown to enhance the yield of the desired furans, as these are extracted to the organic phase prior to further transformation or degradation in the aqueous phase.<sup>1</sup> The use of solid catalysts and of a continuous operation have been indicated as highly relevant for a prospective industrial application.<sup>2</sup> Herein, we report the development of an efficient biphasic process for the conversion of C<sub>5</sub> and C<sub>6</sub> sugars that combines a hybrid heterogeneous catalyst, *i.e.* a mixture of a Lewis-acidic Ga-containing zeolite and Amberlyst-36, and a continuous-flow fixed-bed reactor. We show that the segmented flow established between the two phases considerably enhances the extraction step, thus enabling remarkably high products yields (Fig. 1).



**Figure 1.** Sugar processing in our biphasic segmented-flow fixed-bed reactor (left) and xylose conversion and furfural yield *versus* contact time (right).

1. E.I. Gürbüz, S.G. Wettstein, J.A. Dumesic, *ChemSusChem* **2012**, 5, 383.
2. Y. Román-Leshkov, J.N. Chheda, J.A. Dumesic, *Science* **2006**, 312, 1933.

## Alkane Hydroxylation Using an Artificial Metalloenzyme Based on the Biotin-Streptavidin Technology

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<sup>1</sup>University of Basel

Chemo- and regio-selective alkane hydroxylation is one of the biggest challenges in organic synthesis. While several enzymes display exquisite selectivity, over-oxidation remains a key problem with organometallic catalysts. In natural mono-oxygenases, second coordination sphere interactions provide a selectivity channel, thus ensuring high rates and unrivaled selectivities.

In a biomimetic spirit, we speculated that introduction of a biotinylated oxidation catalyst within streptavidin may afford highly active and selective artificial mono-oxygenases for the hydroxylation of alkanes<sup>[1]</sup>. With this goal in mind, we show that a biotinylated {FeTAML}-moiety (TAML = Tetra Amido Macrocyclic Ligand<sup>[2]</sup>) oxidizes alkanes in the presence of hydrogen peroxide as terminal oxidant. Upon incorporation within various streptavidin mutants, the selectivity can be finely tuned, thus enabling the selective oxidation of various alkanes under physiological conditions.



**Scheme 1.** Artificial Mono-oxygenase results from the incorporation of a biotinylated {FeTAML} moiety within streptavidin.

[1] Michael E. Wilson, George M. Whitesides, *J. Am. Chem. Soc.*, **1978**, 100, 306-307.

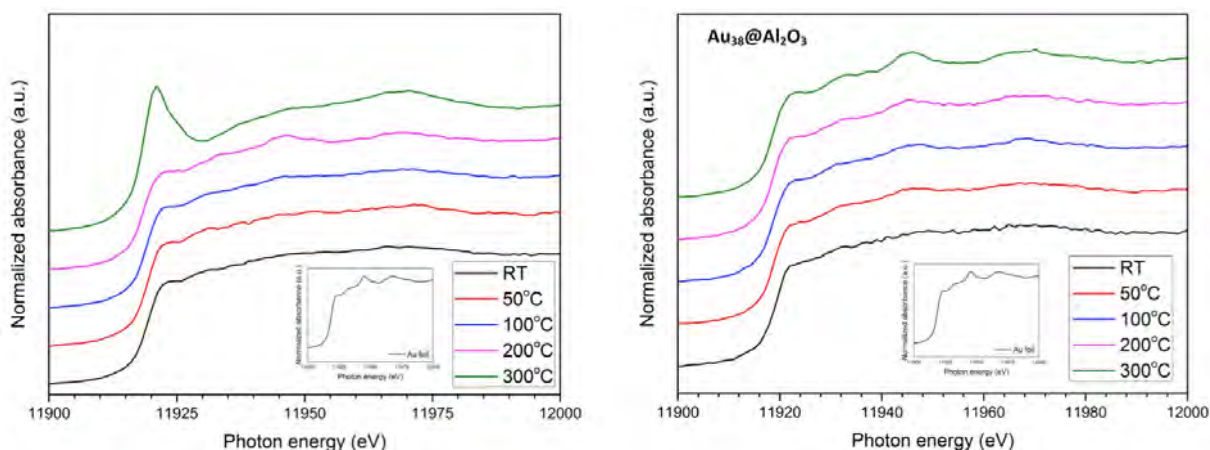
[2] Filipe Tiago de Oliveira, et al., *Science*, **2007**, 315, 835-838.

**Pretreatment effect on supported  $\text{Au}_x(\text{SR})_y$  clusters**

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Thiolate-protected gold nanoclusters ( $\text{Au}_x(\text{SR})_y$ ) have been shown catalytically active and selective in several hydrogenation and oxidation reactions. Although, the gold cluster core is coordinated with thiolate ligands, its configuration provide the stability of the cluster and entail specific properties such as chirality<sup>1</sup>. Previous experience evidences no catalytic activity without the removal of the thiol ligands which implies the loss of properties. One approach represents the partial removal of ligands without losing the structure and properties of the cluster. In order to achieve this, the clusters have been supported on oxides materials and submitted to thermal treatment. Several techniques such as TG, TPD/R/O coupled with mass spectrometry, PM-IRRAS and XAFS have been used to correlate thermal treatment conditions with removal of ligands and cluster stability in these supported systems<sup>2</sup>. The influence of the interaction between the clusters and the support like  $\text{CeO}_2$  and  $\text{Al}_2\text{O}_3$  was also studied. TPD/R/O experiments of 2% wt  $\text{Au}_{38}/\text{Al}_2\text{O}_3$ , showed decomposition of the ligands starting at low temperatures (around 80 °C) with similar fragmentation patterns in different gas atmospheres ( $\text{H}_2$ ,  $\text{O}_2$  and He). It was noted that slightly higher temperatures in the case of  $\text{H}_2$  in comparison with  $\text{O}_2$ , could be related to better stability of the cluster under reduction conditions. Mass spectrometer profiles showed two main maxima around 113 °C and 145 °C that could be assigned to a two steps decomposition of the ligands, related with the two different kinds of staples ( $-\text{S}-\text{Au}-\text{S}-$ ) on the cluster surface. XANESS studies reveal different interaction and stability of the  $\text{Au}_{38}(\text{SR})_{24}$  cluster with a reducible oxide as  $\text{CeO}_2$  and  $\text{Al}_2\text{O}_3$  under thermal treatment.



[1] S.Knoppe,et al., *Angewandte Chemie International Edition*, **2012**, 51, 7589.

[2] Z.Wu,et al., *Journal of the American Chemical Society*, **2014**, 136, 6111.

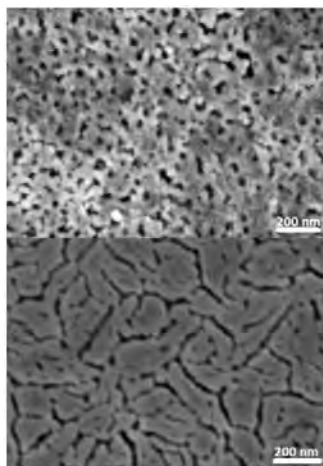
**Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> Nanostructured Composite Photoanode for Water Splitting**

Mario Bärtsch<sup>1</sup>, Sandra Hilaire<sup>1</sup>, Markus Niederberger<sup>1</sup> \*

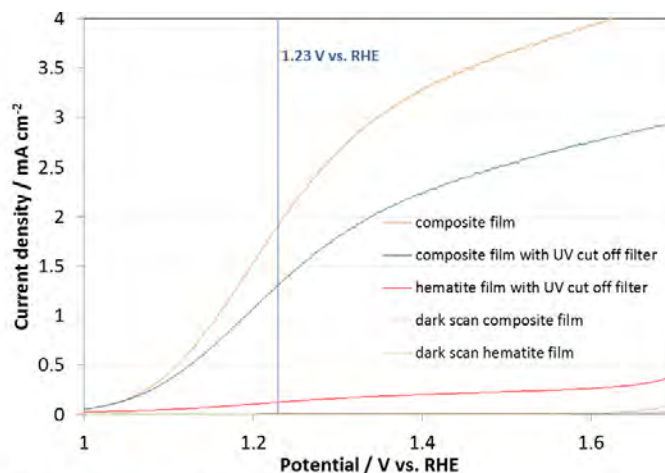
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The demand of green energy has gained great attention in the past few years. Commonly, sunlight is converted into electricity, though the storage thereof is accompanied by losses. This presentation shows an alternative route, leading to hydrogen as a fuel.

We present a Fe<sub>2</sub>O<sub>3</sub> – TiO<sub>2</sub> composite, highly porous thin film made out of a mixed dispersion of titanium and iron oxide nanoparticles. For the synthesis of the nanoparticles, a solvothermal route was pursued. Spin coating of the mixed dispersion on FTO glass substrates leads to a transparent, porous film after annealing. The observed porosity is partially explained by the loss of approximately 50 % of organics after annealing. Incorporation of titania nanoparticles in the Fe<sub>2</sub>O<sub>3</sub> photoanode is accompanied with changes in morphology of the film. According to SEM analysis, the feature size seems to be smaller if titania nanoparticles are used as a secondary compound, compared to pure Fe<sub>2</sub>O<sub>3</sub> films (Fig. 1). For the composite film a photocurrent of 1.91 mA/cm<sup>2</sup> at 1.23 V vs. RHE is obtained under simulated solar AM 1.5 illumination (100 mW/cm<sup>2</sup>) in 1 M NaOH electrolyte solution (Fig. 2).



**Fig 1.** SEM top view images of the composite (top) and pure hematite film (bottom)



**Fig 2.** Photocurrent of the photoanodes

**Activated Carbon Fibers as Efficient Structured Adsorbent for VOCs Removal**Guillaume Baur<sup>1</sup>, Igor Yuranov<sup>1</sup>, Liubov Kiwi<sup>1</sup> \*<sup>1</sup>EPFL Lausanne

Volatile organic compounds (VOCs) are harmful even at low concentrations (1000 ppmv). Adsorption is one of the most efficient methods to control their emissions [1]. Activated carbon fibers (ACFs) are valuable materials due to high SSA (up to 2500 m<sup>2</sup>/g) with a well-defined microporosity combined with open 3D macrostructure and surface functionalities. The high efficiency of ACFs towards non polar VOCs (toluene, benzene) has been demonstrated [2]. However, the adsorption capacity towards oxygenated VOCs is considerably lower due to the absence of polar groups on the surface.

Herein we report that ACF modified by basic oxides nanoparticles (NPs) selectively adsorb acetaldehyde (AA) (model of oxygenated VOCs). AA adsorption was studied by dynamic methods at a short contact time (~40 ms) from diluted AA streams (~1000 ppmv). The metal oxide basicity was found to control the adsorption capacity (see Table).

**Table: Acetaldehyde adsorption capacity for modified ACFs**

Adsorbent	ACF	5% La <sub>2</sub> O <sub>3</sub> /ACF	5% CaO/ACF	5% MgO/ACF	5% Al <sub>2</sub> O <sub>3</sub> /ACF	5% TiO <sub>2</sub> /ACF
Adsorption capacity [w/w %]	3.2	20	18	16	8.5	3.5

The oxides' NPs were mostly below 2 nm and their size is controlled by ACF pores. The heat of AA adsorption was determined by temperature-programmed desorption (TPD). Large adsorption enthalpies indicate on a strong chemical interaction of AA with the adsorbents. All materials were characterized by SEM, HRTEM, TPD and BET methods and results will be presented in details.

**Acknowledgment:** The research described in this abstract was supported by Philipp Morris International.

**Secondary reactions during the decomposition of formic acid**

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Formic acid is considered a feasible compound for alternative energy storage due to its decomposition into hydrogen [1]. Studies of this process focus on the established dehydrogenation ( $\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$ ) and dehydration ( $\text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO}$ ) reactions [2,3], yet seldom explore parallel or succeeding pathways that lead to other products.

The catalytic vapor-phase decomposition of formic acid was carried out over gold supported on  $\gamma$ -alumina. 0.7 wt% Au/ $\text{Al}_2\text{O}_3$  was prepared by DPU [4] and reduced at different temperatures between 100 and 400 °C. Additional experiments with HCHO and  $\text{CH}_3\text{OH}$  as starting materials were carried out.

Formation of secondary products such as HCHO,  $\text{CH}_3\text{OH}$  and  $\text{CHOOCH}_3$  was observed when reacting HCOOH between 100 and 350 °C. Based on the obtained results a reaction scheme describing the formation of these products is proposed. This involves the reduction of HCOOH to HCHO, followed by hydrogenation of HCHO to  $\text{CH}_3\text{OH}$ , which can further react to  $\text{CHOOCH}_3$ . The support or the catalytically active metal was changed to determine whether this reaction scheme is applicable to other catalysts.

[1] Joó F, *ChemSusChem*. **2008**, 1, 805-808.

[2] Gazsi A, Bánsági T, Solymosi F, *J Phys Chem C*. **2011**, 115, 15459-15466.

[3] Ojeda M, Iglesia E, *Angew Chem Int Ed*. **2009**, 48, 4800-4803.

[4] Zanella R, Louis C, *Catalysis Today*. **2005**, 107, 768-777.



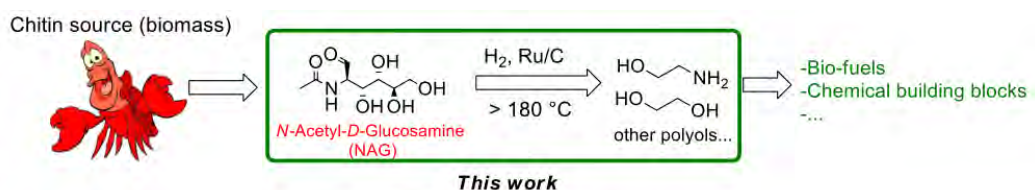
## Towards Ocean Based Biorefinery: N-Acetyl-D-Glucosamine (NAG) to Value-Added Polyols.

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<sup>1</sup>EPFL Lausanne

With depletion of fossil fuels and petrochemical-based feedstocks it is a necessity to find alternative sources of chemicals. Consequently, the conversion of biomass is of great interest, as it is cheap and abundant. Cellulose, which is the main source of biomass, has been successfully converted to small energetic polyols like ethylene glycol (EG), and there is much ongoing research on cellulose conversion.<sup>1,2</sup> We are interested in the conversion of chitin, the closest polymer to cellulose, into valuable chemicals.<sup>3-4</sup>

Herein, we present the results of the first catalytic conversion of *N*-Acetyl-*D*-Glucosamine(NAG), chitin's monomer, into small polyols and *N*-containing molecules, using commercially available heterogeneous transition-metal catalysts in aqueous solution.



[1] Yan, N.; Dyson, P. J. *Current Opinion in Chemical Engineering* **2013**, 2, 178.

[2] Liu, Y.; Luo, C.; Liu, H. C. *Angew Chem Int Edit* **2012**, 51, 3249

[3] Chen, X.; Chew, S. L.; Kerton, F. M.; Yan, N. *Green Chem* **2014**

[4] Zhang, J.; Asakura, H.; Rijn, J. v.; Yang, J.; Duchesne, P.; Zhang, B.; Chen, X.; Zhang, P.; Saeys, M.; Yan, N. *Green Chem* **2014**

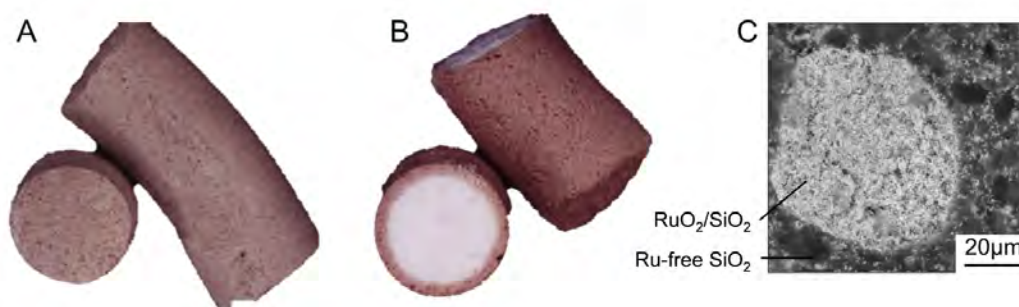


## Controlling the active phase distribution in shaped catalysts

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<sup>1</sup>ETH Zurich

The distribution of active phases on support materials can significantly influence the activity, selectivity, and stability of industrial catalysts.<sup>1</sup> Distribution can be considered on a macroscopic level, covering classical 'homogenous' to 'egg-shell' or 'egg-yolk' scenarios (Fig 1A,B), and on a microscopic level within the shaped body. The latter is crucial since many shaped supports are composite materials (e.g. comprising the carrier and other additives such as binders)<sup>2</sup> and, therefore, the specific interaction of the active phase with the support can strongly impact the catalyst performance (Fig. 1C). To provide greater flexibility and to avoid undesired physicochemical changes, it is often favorable to introduce the active phase by impregnation after the shaping process. For this purpose, it is essential to understand which parameters control the distribution of the active phase or precursor on impregnation of a multi-component support. Taking catalytically-relevant transition metal oxides (e.g. RuO<sub>2</sub>) supported on extrudates of metal oxide composites (e.g. alumina, silica, tin oxide) as model systems, we demonstrate that the surface basicity of the individual phases controls the precipitation of the precursor. Thus, the macroscopic and microscopic distribution of an active phase in a multi-phase system can be tuned by controlling the point of zero charge of the support, surface modifications of the phases, as well as the pH value of the impregnation solution.



**Figure 1.** (A) Homogenous and (B) egg-shell distribution of RuO<sub>2</sub> /Al<sub>2</sub>O<sub>3</sub>. (C) Transmission electron micrograph of RuO<sub>2</sub> /SnO<sub>2</sub>-SiO<sub>2</sub>.

1. A. Gavriilidis, A. Varma, M. Morbidelli, *Catal. Rev.* **1993**, 35, 399.

2. S. Mitchell, N.-L. Michels, J. Pérez-Ramírez, *Chem. Soc. Rev.* **2013**, 42, 6094.

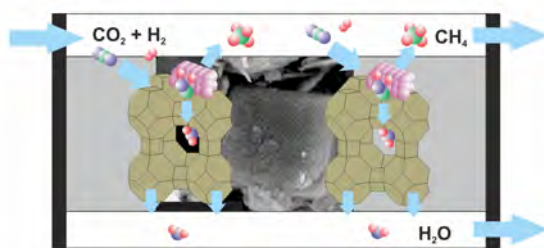
**Membrane reactor concept for CO<sub>2</sub> methanation**

Andreas Borgschulte<sup>1</sup>, Dariusz Burnat<sup>1</sup>, Ulrich Vogt<sup>1</sup>

<sup>1</sup>EMPA Dübendorf

Through imitating the natural carbon cycle, a sustainable energy cycle can be achieved via the production of synthetic hydrocarbons. Their combustion products, water and CO<sub>2</sub>, can be recollected and used as the feedstock for the renewable synthesis of high energy density fuels. Methane is perhaps the most promising such synthetic chemical energy carrier due to the possibility of its integration into the fully developed existing natural gas infrastructure. This strategy comprises an entirely new concept of energy fluxes and has resulted in active investigations to discover green, efficient and cheap solutions to span the gap between energy demand and renewable energy supply ("power-to-gas").

We recently demonstrated the concept of increasing the conversion yield of CO<sub>2</sub> methanation via so-called sorption-enhanced catalysis [1]. The principle of sorption-enhancement relies on the use of an appropriate catalytic support, e.g. a zeolite, which serves as an effective sink for specific gas phase products of the desired reaction, e.g. water, thereby pushing the reaction in the direction of choice. The active removal of water from the reaction centers at the Ni sites shifts the reaction equilibrium towards the products and thereby enhances the conversion yield while suppressing side products such as CO. However, a drawback of the concept is that the sorption catalysts have to be regenerated regularly requiring a new reactor design (a quasi-continuous multi-plate reactor), which is being developed currently. Alternatively, the sorption catalyst is implemented into a membrane. The methanation reaction takes place on one side of the membrane, which is simultaneously dried from the other ("membrane reactor concept"). We present the preparation of catalytically active membranes with emphasis on the physico-chemical characterization of the membranes, i.e. microstructure, internal surface area, and the permeability of hydrogen and water. We demonstrate the proof-of concept of the membrane reactor for CO<sub>2</sub> methanation.



[1] Andreas Borgschulte, Noris Gallandat, Benjamin Probst, Riccardo Suter, Elsa Callini, Davide Ferri, Yadira Arroyo, Rolf Erni, Hans Geerlings and Andreas Züttel, *Phys. Chem. Chem. Phys.*, 2013,15, 9620.

**Activation of Cu-mordenite for methane to methanol conversion: Effects of synthesis and multiple cycles on methanol production**

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<sup>1</sup>ETH Zurich and Paul Scherrer Institute, Villigen, <sup>2</sup>Paul Scherrer Institute, Villigen, <sup>3</sup>ETH Zurich

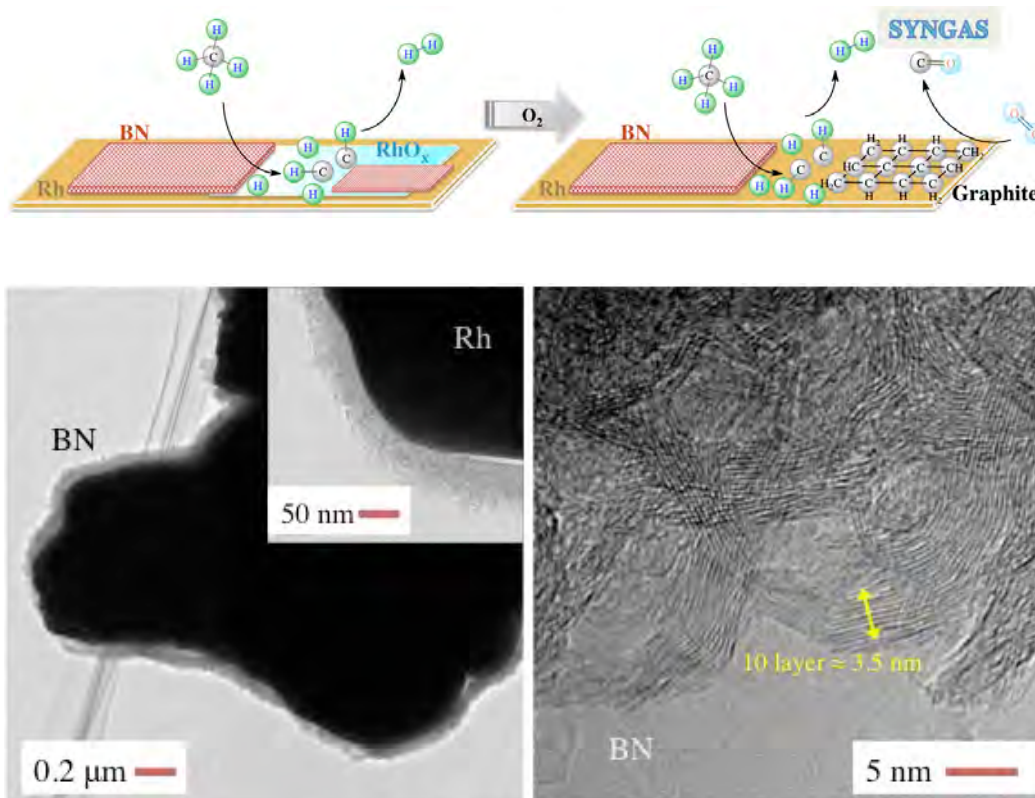
Cu-mordenite catalysts are promising candidates towards the selective conversion of methane to methanol at relatively low temperatures. Using these catalysts, the production of methanol involves a multi-step process involving activation of the catalyst in O<sub>2</sub>, where metal-oxygen species are formed. This is followed by reaction with CH<sub>4</sub>, in which oxygen-metal sites react with CH<sub>4</sub> to form a chemisorbed oxidized intermediate, which is probably a methoxy species bound to the active site and extractable in water at room temperature. This multi-step process stabilizes the intermediate, preventing over-oxidation to CO<sub>2</sub>. Cu-MOR catalysts prepared using aqueous (CuMOR<sub>A</sub>) and solid state ion exchange (CuMOR<sub>S</sub>) routes showed improved activity towards methanol production when multiple process cycles were employed. For CuMOR<sub>A</sub>, the amount of methanol produced increased by 40% reaching 17.8 μmol methanol / g catalyst after the second cycle and remained constant after subsequent cycles. Methanol production reached a maximum (22.6 μmol methanol / g catalyst) at the 5<sup>th</sup> cycle when CuMOR<sub>S</sub> was used and significantly higher methanol per Cu values were obtained as compared to CuMOR<sub>A</sub>. X-ray diffraction and transmission electron microscopy show that crystal structure and morphology of the catalysts remained similar with subsequent cycles. On the other hand, N<sub>2</sub> adsorption data showed decreased BET surface area at the end of the multiple process cycles for both catalysts suggesting pore blockage due to Cu clustering. This is supported by X-ray absorption spectra of CuMOR<sub>S</sub> showing elimination of a nearby light scatterer, most probably chlorine, and simultaneous increase in magnitude of a heavier scatterer, probably copper, in the first three cycles where significant increase in methanol was observed. These observations suggest that cyclic operation changes the dispersion of Cu, possibly increasing the amount of active Cu sites, thereby increasing the amount of methanol produced per cycle.

## Protecting nano-particles against sintering for application under demanding catalytic conditions

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<sup>1</sup>Paul Scherrer Institute, Villigen, <sup>2</sup>ETH Zurich and Paul Scherrer Institute, Villigen

A general problem of performing catalysis under harsh conditions, such as high temperature is the sintering of the catalytically active component. One such reactions is methane oxidation to synthesis gas, which is of continuing interest for conversion of natural gas to hydrogen respectively valuable chemicals. While noble metals, such as platinum and rhodium, show excellent catalytic ability, metal agglomeration and carbon deposition cause partially irreversible deactivation [1]. We demonstrate a method to synthesize a protective layer of h-BN on polycrystalline rhodium nano-particles [2] and show that these covered particles are active and stable for methane oxidation. The synthesis, catalytic activity, and factors affecting the reaction activity of BN-rhodium metal catalyst will be presented. These results illustrate the potential of using BN on metal catalysts to develop a next generation of stable, highly active, and selective catalysts, while not explored yet.



[1] Bharadwaj, S. S.; Schmidt, L. D. *Fuel Process. Technol.* **1995**, 42, 109-127..

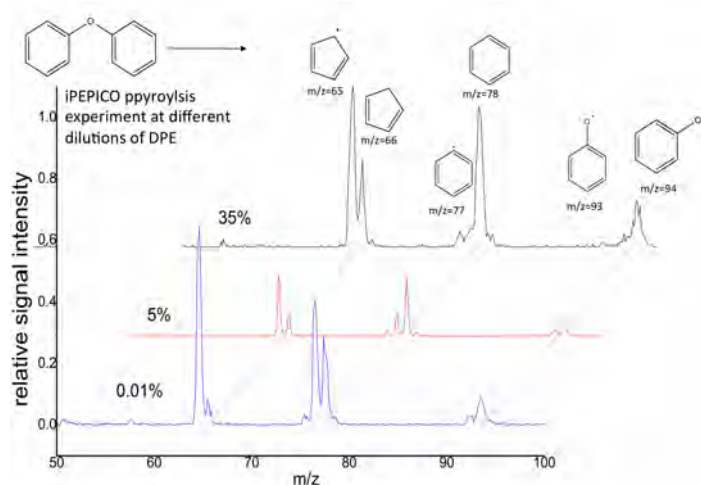
[2] Dil, H.; Lobo-Checa, J.; Laskowski, R.; Blaha, P.; Berner, S.; Osterwalder, J.; Greber, T. *Science* **2008**, 319, 1824-1826

## The Mechanism of (catalytic) Lignin Pyrolysis: Linking Model Compounds to Lignin

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Pyrolysis is one of the most promising methods to convert lignin into useful stock chemicals. In the presence of catalysts, high yields of aromatic products can be obtained.<sup>1</sup> The mechanism of (catalytic) pyrolysis, however, is still unclear and difficult to study, since the lignin as starting material is highly irregular and also varying with bio-resource and separation method.<sup>2</sup> Thus model compounds mimic certain substructures and bondings of the real lignin and represent a known starting structure.<sup>3,4,5</sup> We recently published the decomposition mechanism of diphenylether (DPE) and guaiacol in different experimental setups, ambient pressure and collision reduced conditions at the VUV-beamline, to be able to correlate the observed products to primary decomposition pattern.



Primary radicals either decompose or rearrange depending on the reaction environment. Interestingly, different degrees of dilution in the iPEPICO-setup showed varying signal intensities of secondary reaction products, such as dibenzofurane, which indicates a bimolecular mechanism. With increasing concentration less stable radicals become less frequent. This is consistent with our observation that the lignin forming more stable radicals has a lower yield in char. The stability of the formed radicals is also crucial for the resulting product selectivity. The temperature dependency of the product distribution of both model compounds and real lignin correlate, thus the same mechanisms are dominant. The unique combination of model studies under idealized conditions and pyrolysis under realistic conditions provide new insights into the mechanism of lignin pyrolysis, which is needed to improved processes that yield bio-fuels and / or -chemicals.

[1] Ma, Z., Troussard, E. & van Bokhoven, J. a. *Appl. Catal. A Gen.* **2012**, 423-424, 130-136

[2] Britt, P. F., Buchanan, A. C. & Evans, R. J. **2008**, 47, 395-397

[3] Scheer, A. M., Mukarakate, C., Robichaud, D. J., Nimlos, M. R. & Ellison, G. B. *J. Phys. Chem. A* **2011**, 115, 13381-9

[4] Scheer, A. M. *et al. J. Chem. Phys.* **2012**, 136, 044309

[5] Shin, E.-J., Nimlos, M. R. & Evans, R. J. *Fuel* **2001**, 80, 1689-1696

## Esterification of Lignin Monomers and Fatty Acids using Separable Solid Acids

Bahir Duraki<sup>1</sup>, Xiwei Xu<sup>1</sup>, Jeroen A. van Bokhoven<sup>1</sup> \*

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Esterification is an important reaction in the chemical industry. Biodiesel is produced by esterification of fatty acids with methanol using a solid catalyst and high temperature<sup>1</sup>. Lignin is a promising, renewable, and oxygen-rich resource for phenol and phenol-derivative compounds. Pyrolysis of lignin yields bio-oil and contains the monomers and dimers of the parent lignin. However, the properties of bio-oil are disadvantageous and contain too many compounds to afford separation<sup>2</sup>. Our idea is to chemically catch the oxygen-rich lignin monomers and react them to produce new chemicals. This can be done by esterification and acylation with another biomass resource, a long chain fatty acid. These acid-catalyzed reactions were tested using commercial zeolites, modified with heteroatoms and after being made mesoporous<sup>3</sup>, however, these gave unsatisfactory results.

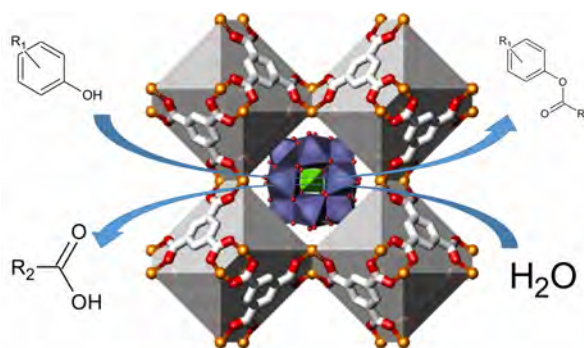


Figure 1: HPW/Cu<sub>3</sub>(BTC)<sub>2</sub>: Keggin ion (W-octahedra blue, P-tetrahedron green) in HKUST-1 framework (carbon: white, oxygen: red, copper: orange). Using Keggin ion for the esterification reaction gives 25 % ester yield, an acid conversion of 32 % and selectivity to acid of 73 %. Using HPW/Cu<sub>3</sub>(BTC)<sub>2</sub> gives 4%, 33% and 12 %, respectively. Using only the HKUST1 framework as catalyst, no yield and conversion was observed. The illustration is from ref. [4].

Poly-oxo metallate as HPW show high promising activity towards the esterification of alcohols and acids. To overcome the poor dissolution of HPW in polar solvents, a core-shell catalyst containing HPW was synthesized, using HKUST-1. This catalyst shows good esterification and acylation yields for small molecules<sup>4</sup>. Using more complex molecules as they are typically produced from lignin pyrolysis, afforded reasonable, but slightly lower yields. The combination of HPW with hollow silicate as protecting unit shows low ester yield. It was shown that the phenol-derivative is inert towards this highly reactive catalyst.

[1] Shih-Yuan C., Takehisa M., Yohko A., Makoto T., Yoshimura Y., *Applied Catalysis B: Environmental* **2007**, 148-149, 344-356.

[2] Zhao C., Lercher J. A., *ChemCatChem* **2012**, 4, 64-68.

[3] Ordonsky V. V., Ivanova I. I., Knyazeva E. E., Yuschenko V. V., Zaikovskii V. I. *Journal of Catalysis* **2012**, 295, 207-216.

[4] Wee L. H., Janssens N., Kirschhock E. A., Martens J. A. *Catalysis Today*, **2011**, 171, 275-280.



## Increased methanation activity of ruthenium nanoparticles through passivation of the silica support

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<sup>1</sup>ETH Zurich

Improving the catalytic performances of supported metal nanoparticles (NPs) is an intense area of research, which focuses on modulating the size and the shape of the metallic NPs, but also their interaction with the support surface.<sup>1,2,3</sup> This study shows that the introduction of passivating groups (-OSi(Me)<sub>2</sub>**R** with **R**= **Me** or **Bu**) at the interface between the support surface (silica) and RuNPs increases the rate of the reaction on RuNPs (per mole of surface Ru atoms) by a factor 5-6 compared to silica-supported RuNPs, whose surface is exposed to silanols. Chemisorption, IR spectroscopy and temperature programmed desorption tests indicate that the rate increase originates from the lower CO affinity of RuNPs supported on passivated silica.

[1] Cargnello, M.; Doan-Nguyen, V.V.T.; Gordon, T. R.; Diaz, R. E.; Stach, E. A.; Gorte, R. J.; Fornasiero, P.; Murray, C. B. *Science* **2013**, *341*, 771.

[2] Baker, R.L.; Kennedy, G.; Van Spronsen, M.; Hervier, A.; Cai, Xiaojun.; Chen, Shiyu.; Wang, L-W.; Somorjai, G.A. *J. Am. Chem. Soc.* **2012**, *134*, 14208.

[3] Farmer, J. A.; Campbell, C. T. *Science*, **2010**, *329*, 933.



## Identifying short-lived phases and their rates of formation and disappearance from transient XAS spectroscopy

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The oxidation of carbon monoxide over platinum group metals can proceed in various reaction regimes, depending on temperature and reactant concentrations. Two of these are well known and characterized: a low temperature, low activity state with CO covered metal surface, and a high temperature, high activity state with an oxidic surface. In contrast, the structure of the catalyst during the transition between these two regimes is strongly debated in the literature<sup>[1]</sup>. Its short-lived nature hampers its detection.

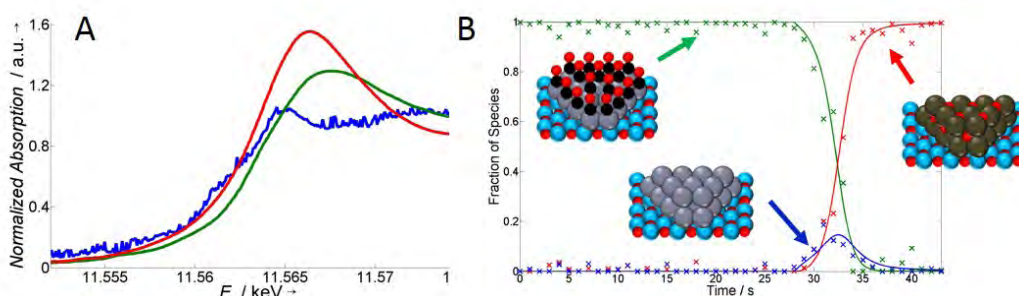


Figure 1: Pt-L<sub>3</sub> edge XANES spectra of CO covered platinum (green), oxidized platinum (red) and the isolated intermediate spectrum (A), as well as the concentrations over time and proposed structures (B).

We induced the transition between the two reaction regimes by changing the concentration of reactants in the feed and detected the structural changes during the switch by using time-resolved XAS spectroscopy. Principle component analysis and kinetic analysis of the resulting spectra showed the formation and disappearance of an intermediate species. The spectrum of the intermediate species could be isolated and was identified as that of adsorbate-free platinum surface.

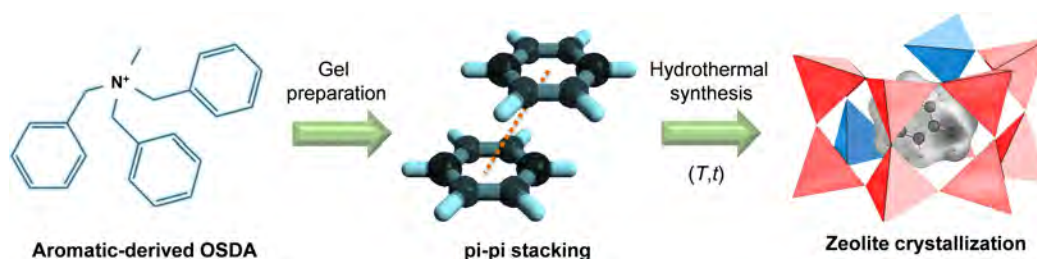
[1] a) R. van Rijn, O. Balmes, R. Felici, J. Gustafson, D. Wermeille, R. Westerström, E. Lundgren, J. W. M. Frenken, *The Journal of Physical Chemistry C* **2010**, 114, 6875-6876; b) F. Gao, Y. Wang, D. W. Goodman, *The Journal of Physical Chemistry C* **2010**, 114, 6874-6874.

## Studying the structure-directing effect of aromatic-functionalized templates in zeolite synthesis

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The identification of new zeolite framework types is of great interest, since the specific topology and properties of their microporous structure gives rise to the unique shape selective character responsible for their wide success as catalysts and sorbents. One of the most important approaches to obtain new zeolites is the use of specifically-tailored organic structure directing agents (OSDAs) to guide the assembly of oxides of silicon and/or other elements like Al, B, Ti, Ge during their synthesis. In the presence of aromatic-functionalized OSDAs,  $\pi$ - $\pi$  interactions between aromatic rings in neighboring molecules can result in long-range directing effects ('supramolecular self-assembled molecules'),<sup>1</sup> which can promote the crystallization of new zeolite structures. Here, we synthesize novel aromatic quaternary ammonium cations to explore their application to access diverse zeolite phases.



**Figure 1.** Structure-directing effect of aromatic OSDAs in zeolite synthesis.

1. A. Corma, F. Rey, J. Rius, M. Sabater, S. Valencia, *Nature* **2004**, 431, 287.

Florent Héroguel<sup>1</sup>, Georges Siddiqui<sup>1</sup>, Olga V. Safanova<sup>2</sup>, Mike D. Detwiler<sup>3</sup>, Dmitry Y. Zemlyanov<sup>3</sup>, Christophe Copéret<sup>1</sup> \*

Aluminosilicates are the most used catalysts and catalyst supports. Together with metal nanoparticles, amorphous silica-aluminas (ASA) provide bi-functional catalysts, which exploit the mild acidity of ASA and the hydrogenation / hydrogenolysis properties of metal nanoparticles.

In this study, we apply the concepts of Surface Organometallic Chemistry (SOMC)[1] to the controlled growth of iridium nanoparticles on silica and alumina.[2] On the latter, the metal-support interface is tuned upon decomposition of a well-defined dimeric supported iridium siloxide (figure 1), with the formation of a silicon aluminate layer conferring mild acidity to the materials. The particles display all the desired properties for applications in catalysis, thanks to the use of organometallic precursors: they are small (0.5 nm), narrowly dispersed, with a homogeneous spatial distribution and the absence of large metal aggregates and pollution of the metal surface with residual ligands.

We present the synthesis of the materials as well as their detailed characterization at every step using molecular and surface science techniques such as NMR and FTIR spectroscopies, TEM, XAS, XPS, as well as chemisorption. Finally, catalytic results probing the materials bifunctionality are discussed.

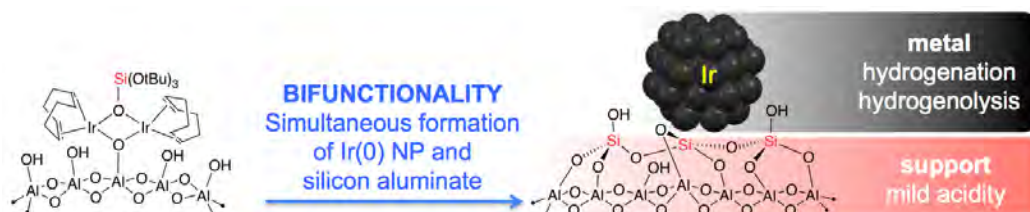


Figure 1. Simultaneous formation of iridium particles and Si-Al mixed oxide on alumina.

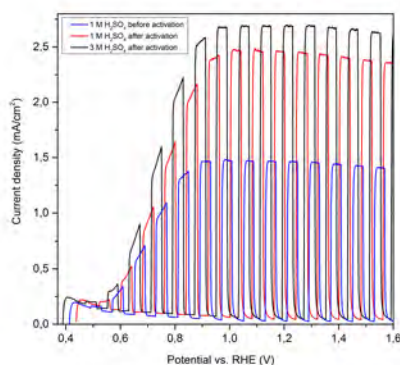
- [1] Christophe Copéret, Florent Héroguel, Recent advances in Surface Organometallic Chemistry, in "Applied Homogeneous Catalysis with Organometallic Compounds". 3<sup>rd</sup> edition, Ed. B. Cornils, W. A. Herrmann, M. Beller, R. Paciello, **2014**, Wiley-VCH.
- [2] Florent Héroguel, Dominique Gebert, Michael D. Detwiler, Dmitry Y. Zemlaynov, David Baudouin, Christophe Copéret, *J. Catal.* **2014** (under revision).

## Microwave-assisted nonaqueous synthesis of WO<sub>3</sub> nanoparticles for crystallographically oriented photoanodes for water splitting

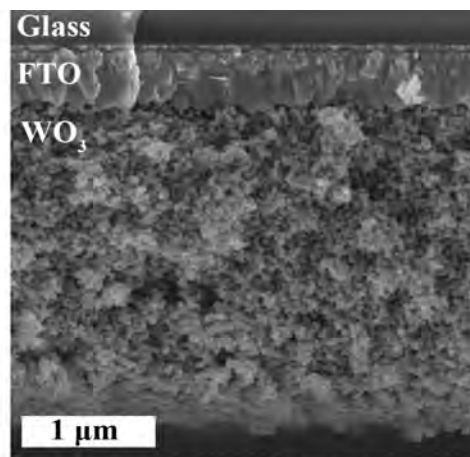
Sandra Hilaire<sup>1</sup>, Martin J. Süess<sup>2</sup>, Niklaus Kränzlin<sup>1</sup>, Krzysztof Bieńkowski<sup>3</sup>, Renata Solarska<sup>3</sup>, Jan Augustyński<sup>3</sup>, Markus Niederberger<sup>1</sup> \*

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Nanostructured WO<sub>3</sub> photoanodes with crystallographic orientation along the [001] direction were fabricated via doctor blading nanoparticles synthesized through a microwave-assisted nonaqueous sol-gel route. Monoclinic WO<sub>3</sub> platelets with a size ranging from 20 to 40 nm and a thickness of 3 nm were obtained after a short reaction time of 10 minutes under microwave irradiation. No organics were present on the surface of the nanoparticles after synthesis. The films consisted of a porous network of nanoparticles and their photoelectrochemical activity was tested. After activation of the surface by a cathodic polarization of the photoanodes in the dark which led to a significant increase of photocurrent, the films exhibited a maximum photocurrent of 2.7 mA/cm<sup>2</sup> at 1 V vs. reversible hydrogen electrode (RHE) in 3 M H<sub>2</sub>SO<sub>4</sub> under simulated AM 1.5 G illumination (100 mW/cm<sup>2</sup>) comparable to the best photocurrents ever reported for WO<sub>3</sub> photoanodes.[2,3] Incident photon-to-current measurements showed a photoconversion of the photoanodes reaching 70% in 3 M H<sub>2</sub>SO<sub>4</sub>. In comparison to the chemical solution growth of films from molecular precursors, the use of preformed nanoparticles in form of powders is not only more robust and easier to up-scale, but offers many opportunities to improve the photoelectrochemical performance by tailoring the nanoparticle size, the shape, and their arrangement on the substrate.



Photocurrent density of a WO<sub>3</sub> photoanode in 1 M H<sub>2</sub>SO<sub>4</sub> before (blue) and after (red) cathodic activation and in 3 M H<sub>2</sub>SO<sub>4</sub> after cathodic activation (black) under AM 1.5 chopped illumination (100 mW/cm<sup>2</sup>).



SEM cross-section view of a WO<sub>3</sub> photoanode

[1] Sandra Hilaire *et al.*, **2014**, submitted.

[2] Renata Solarska, R. Jurczakowski and Jan Augustynski, *Nanoscale*, **2012**, 4, 1553-1556.

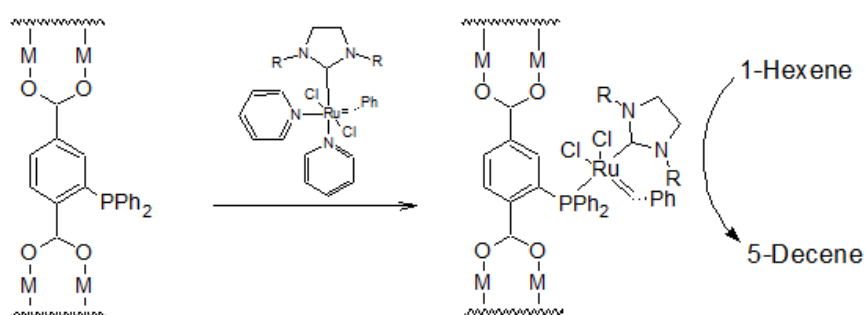
[3] B. Marsen, E. L. Miller, D. Paluselli and R. E. Rocheleau, *International Journal of Hydrogen Energy*, **2007**, 32, 3110-3115.

## Organometallic Chemistry with Metal-Organic Frameworks: Well-Defined Heterogeneous Catalytic Sites for Olefin Metathesis

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Metal-organic frameworks (MOFs) are crystalline materials formed by the self-assembly of organic linker units with metallic nodes. The ability to tune the porosity and functionality by modifying the organic and inorganic precursors, increase their prospective applications.[1] The synthesis of phosphine-functionalized MOFs opened up a wide array of possibilities in single site heterogeneous catalysis.[2] The coordination of molecular organometallic complexes to these well-defined sites can be used to immobilize catalysts and spatially confine them inside the pores of the framework.



Here, we report the synthesis of the phosphine functionalized MIL-101-(Al)-NH<sub>2</sub> structure [3] and its use as a solid ligand for coordination of a Grubbs catalyst. The coordination of the ruthenium complex to the phosphine sites will be investigated using solid state <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy. This heterogeneous material catalyzed the self-metathesis reaction of 1-hexene. This reactivity demonstrates the proof of concept and illustrates the catalytic potential of phosphine-modified MOFs.

[1] J. Rowsell, O. M. Yaghi, *Microporous Mesoporous Mater.* **2004**, 73, 3-14.

[2] J. Vaclavik, M. Servalli, C. Lothschutz, J. Szlachetko, M. Ranocchiari, J. A. van Bokhoven, *ChemCatChem*, **2013**, 5, 692-696.

[3] F. L. Morel, M. Ranocchiari, J. A. van Bokhoven, *Ind. Eng. Chem. Res.*, **2014**, in press.

**Structure modification and carbon resistance improvement of modified Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for synthetic natural gas production**

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<sup>1</sup>Paul Scherrer Institute, Villigen, <sup>2</sup>Foundation of Research and Technology-Hellas, Institute of Chemical Engineering and High-Temperature Chemical Processes (FORTH/ICE-HT), Patras, Greece, <sup>3</sup>EMPA Dübendorf, <sup>4</sup>Paul Scherrer Institute, Villigen and EPFL Lausanne

The conversion of biomass to energy carriers like CH<sub>4</sub> through CO methanation reaction is a desirable route towards development of efficient energy production/conversion systems. Ni/Al<sub>2</sub>O<sub>3</sub> is considered the state-of-the-art catalyst for this application. However, it suffers from deactivation due to carbon deposition, caused mainly by hydrocarbons (e.g. C<sub>2</sub>H<sub>4</sub>) that are present in the feed. In this work, M-modified Ni/Al<sub>2</sub>O<sub>3</sub> catalysts were synthesized by impregnating M and Ni on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (M: Mg, Ca, Ba, B, Ga or Rb) [1]. The activity for CO methanation was evaluated in a fixed-bed reactor using 25 vol% H<sub>2</sub>-5 vol% CO in N<sub>2</sub> (GHSV= 118000 mLg<sup>-1</sup>h<sup>-1</sup>). The stability tests were conducted in the presence of 2000 ppm C<sub>2</sub>H<sub>4</sub>, whereas the amount/type of carbon deposits was estimated by TPO. Ni/Al<sub>2</sub>O<sub>3</sub> lost ~20% of its initial activity at 320°C in the first 4 h in the presence of C<sub>2</sub>H<sub>4</sub>. The stability of Ni/Al<sub>2</sub>O<sub>3</sub> was greatly enhanced by the addition of low amount of M, which did not exhibit any activity loss. TPO of the spent catalysts indicates that the amount and type of carbon deposits change upon addition of M (inset of Fig. 1). No nickel carbide, amorphous and polymeric carbon are detected on M-Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, that are characterized by the low temperature TPO signal. The latter is considered crucial for catalysts deactivation in both fixed-bed and fluidized-bed reactors. The origin of the enhanced catalytic performance arises likely from the structural modifications observed in the Ni phase upon modification. Electron microscopy reveals that Ni domains exist with lattice distortions/dislocations, whereas the intimate contact between M and Ni are evidenced by NMR and Raman spectroscopy. These structural modifications seem to be unfavorable for the formation of carbidic nickel and/or amorphous carbon.

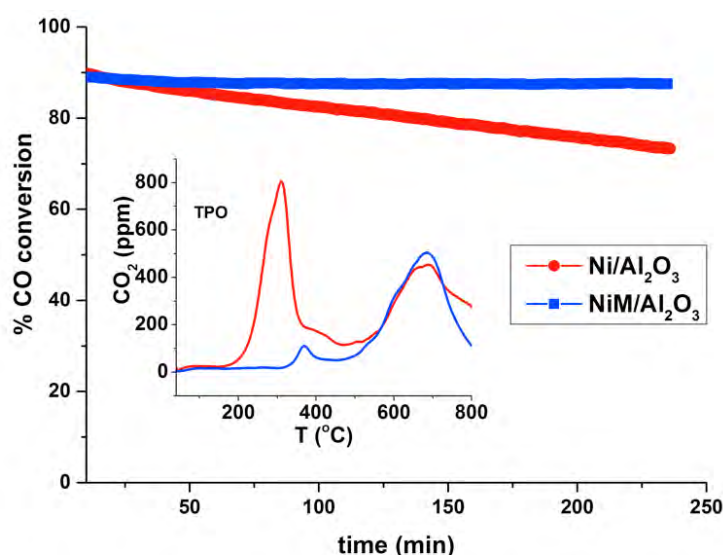


Fig. 1: Stability test at 320°C in the presence of C<sub>2</sub>H<sub>4</sub> and TPO (inset graph)

[1] A.Kampilis, T. J. Schildhauer, O. Kröcher, *Patent application in progress*.



## Hydrogenation of Arenes by Metal Nanoparticles Combined with Lewis Acidic Ionic Liquids

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Ionic liquids (ILs) present favourable media and support for immobilized nanoparticles providing rotational freedom and access to the entire surface of a nanoparticle. Moreover, functionalized acidic ILs can work cooperatively with metal nanoparticles in catalytic reactions [1,2].

A novel catalytic system composed of rhodium nanoparticles dispersed in BMimBF<sub>4</sub> ionic liquid and Lewis acidic chlorozincate ILs has been developed. In order to evaluate Lewis acidity we used a method based on IR spectroscopy with a nitrile-functionalized IL probe (Fig. 1). IL speciation was also determined by Raman spectroscopy (Fig. 2). The metal incorporated in an ionic liquid and the ratio of metal chloride:organic salt used for its synthesis are the main factors influencing Lewis acidity of chlorozincate ILs [3]. The Rh-chlorozincate combined catalysts were found to be highly effective in the reactions of hydrogenation of arenes and phenol. The conversion was considerably enhanced with the addition of chlorozincate ILs and the excellent correlation of catalytic results and IR and Raman IL speciation data was observed.

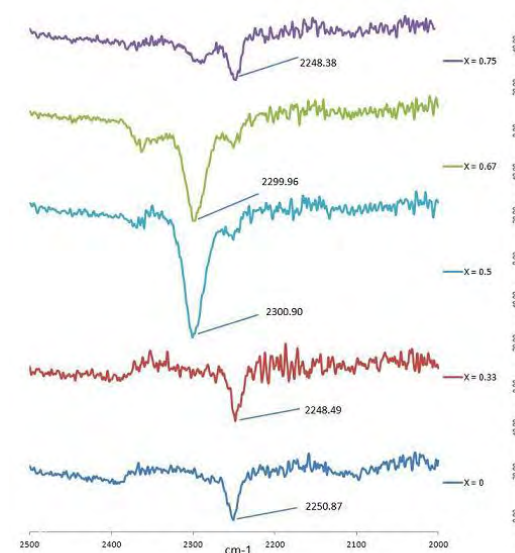


Fig. 1

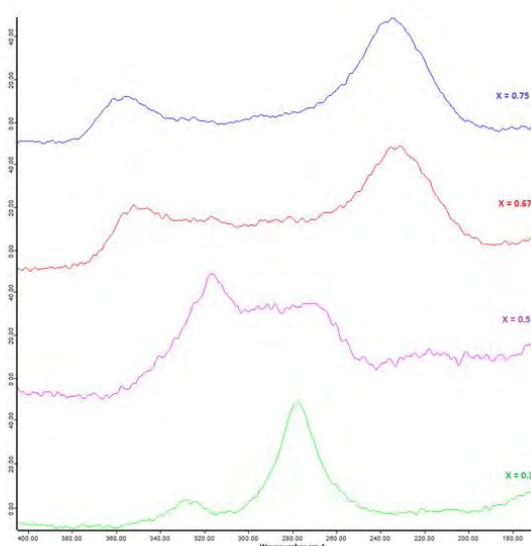


Fig. 2

[1] R. Deshmukh, J.W. Lee, U. S. Shin, J. Y. Lee, C. E. Song. *Angew. Chem. Int. Ed.* **2008**, 47, 8615-8617.

[2] N. Yan, Y. Yuan, R. Dykeman, Y. Kou, P. J. Dyson. *Angew. Chem. Int. Ed.* **2010**, 49, 5549-5553.

[3] J. Estager, J. D. Holbrez, M. Swadźba-Kwaśny. *Chem. Soc. Rev.* **2014**, 43, 847-886.



## Single particle spectroscopy on well-defined models systems prepared using nanotechnology to study size-effects in catalysis

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<sup>1</sup>ETH Zurich and Paul Scherrer Institute, Villigen, <sup>2</sup>Paul Scherrer Institute, Villigen, <sup>3</sup>ETH Zurich

Understanding size effects of nanoparticles on catalysis is of great interest and many studies have indicated that shape and size of nanoparticles considerably effect catalytic activity [1]. Their synthesis in a controlled manner resulting in well-defined shape and size as well as their study at the single particle level will help gaining deeper insight into chemical mechanisms and elucidating size and shape effects. The mechanism of oxidation of iron has extensively been investigated and studies have concluded that the behavior of bulk iron is different from nanoparticles [2]. Well-defined model systems consisting of ordered single iron nanodots of different sizes in the nano-meter size domain in a  $5 \times 5 \mu\text{m}^2$  field-of-view was achieved using top-down nanofabrication (Fig. 1(a)). X-ray photoemission electron microscopy (PEEM) enables measuring the structure of individual iron particles.

We performed simultaneous microscopy and spectroscopy on all different sizes under the same conditions to visualize the elemental contrast images and study the size effect during the reduction of surface oxide and oxidation of the iron nanodots. Fig. 1(b) illustrates x-ray absorption spectroscopy (XAS) measurements on a single nanodot of 60 nm during different intervals of oxygen dosage and similar time-dependent evolution of oxide has been analyzed for all sizes. Using principal component analysis and fitting reference XAS spectra, we have compared the oxidation rates and composition for different sizes. We observed phase transformation from FeO to Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> with different rates as a function of size (shown for a 40 nm dot in Fig 1 (c)). Based on the kinetics and thermodynamic stability of the different oxides, activity of different sizes is compared and a reaction mechanism for the inter-conversion of oxides in iron nanoparticles and oxide formation is suggested.

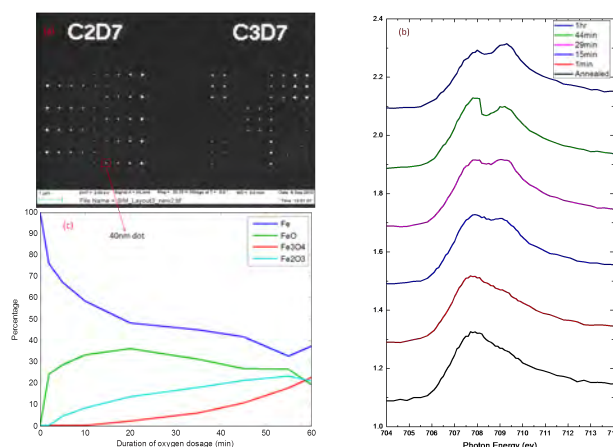


Fig. 1: (a) SEM image showing iron nanodots with diameters of 6, 8, 10, 30, 40, 60, and 80 nm with distance of 500 nm between particles. (b) Evolution of oxide peak for 60nm dot for 1 hour of oxygen dosage. (c) Development of individual oxide components for a single 40 nm dot.

[1] M. Shekhar, F. H. Ribeiro, *Journal of the American Chemical Society*, **2012**, 134, 4700-4708

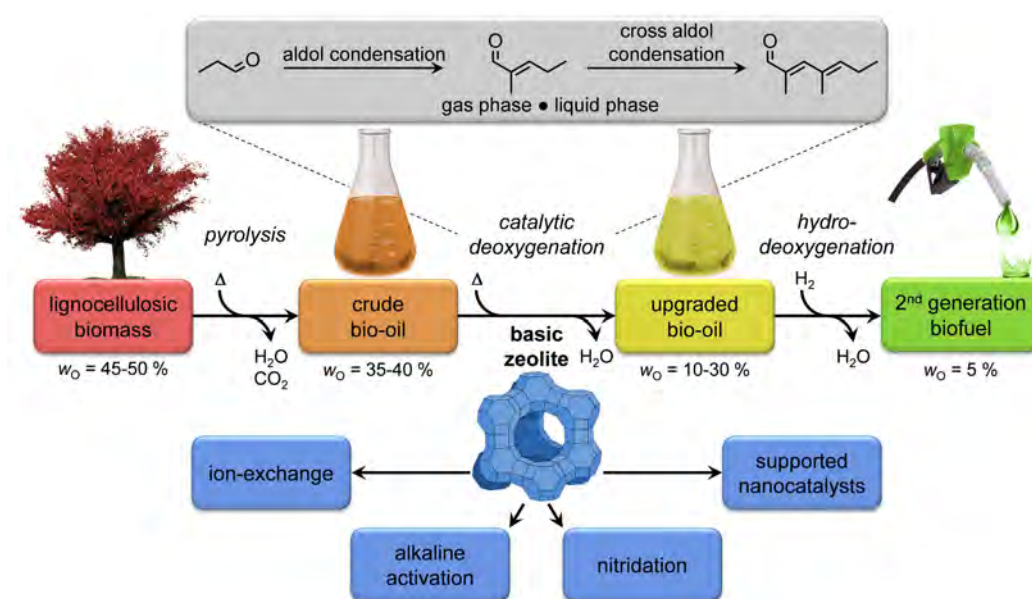
[2] W. Feitknecht, K. J. Gallacher, *Nature*, **1970**, 228, 548-549

## Post-synthetic design of basic zeolites for bio-oil upgrading

Tobias Keller<sup>1</sup>, Elodie Gonçalves Rodrigues<sup>1</sup>, Sharon Mitchell<sup>1</sup>, Javier Pérez-Ramírez<sup>1</sup> \*

<sup>1</sup>ETH Zurich

Eco-friendly, sustainable fuels can be derived from lignocellulosic biomass *via* liquefaction by pyrolysis, provided that the oxygen content of the obtained crude bio-oil is substantially reduced.<sup>1</sup> Since the direct hydrodeoxygenation requires an excessive hydrogen consumption, an intermediate catalytic deoxygenation represents a promising alternative (Fig. 1). Aldol condensations carried out over basic catalysts are particularly attractive for this purpose, as they enable oxygen removal in the form of water from the large aldehyde fraction of bio-oil. However, control over basic strength and selectivity is crucial to prevent over-activation of the substrate. We investigate the effectiveness of basic zeolites in both the liquid- and gas-phase self-condensation of propanal as a model reaction. A platform of high-silica zeolites is prepared by traditional and state-of-the-art approaches. The control over the amount and strength of basic sites is compared not only for ion-exchanged, alkaline-activated, and nitrided zeolites, but also for zeolite-supported MgO, hydrotalcite, and hydroxyapatite nanocomposites. Post-synthetic modification of the zeolite enables the fine-tuning of their mesoporosity, leading to an enhanced dispersion of the supported active phases and accessibility of the active centers. Tailored FAU-type zeolites stand as the most active and stable catalysts for prospective applications in bio-oil upgrading.



**Figure 1.** Intermediate catalytic deoxygenation of pyrolysis oil over basic zeolite catalysts.

1. M. Stöcker, *Angew. Chem., Int. Ed.* **2008**, 47, 9200.

2. T.C. Keller, E.G. Rodrigues, J. Pérez-Ramírez, *ChemSusChem* **2014**, doi:10.1002/cssc.201301382.

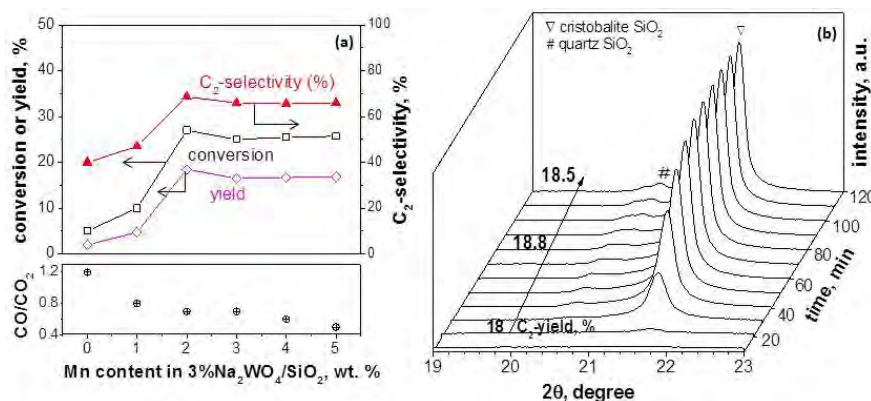
## Oxidative coupling of methane on flame-made Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>: Influence of catalyst composition and reaction conditions

Rajesh Koirala<sup>1</sup>, Robert Büchel<sup>1</sup>, Sotiris E. Pratsinis<sup>1</sup>, Alfons Baiker<sup>1</sup> \*

<sup>1</sup>ETH Zurich

Ethylene, an industrially valuable compound, can be synthesized by oxidative coupling of methane (OCM) in a single pass reaction using natural gas, in contrast to current production by cracking naphtha and gas-oil [1, 2]. Among wide range of catalysts reported, multicomponent Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> has been of great interest due to its high activity and selectivity [3]. However, the reaction remains a challenge due to the still limited C<sub>2+</sub>-yield achieved and the lack of a complete understanding of the relation between catalyst properties and reaction conditions and their influence on reaction performance [4]. Therefore, further understanding regarding influence of the composition and structural properties is required for advancing such catalysts to industrial application.

So various compositions of Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalysts (0-5 wt% Mn and 0-6 wt% Na<sub>2</sub>WO<sub>4</sub>) were made by flame spray pyrolysis (FSP) [5]. These were characterized and tested for the OCM reaction in a continuous flow microreactor at different reaction conditions (temperature, CH<sub>4</sub>/O<sub>2</sub> feed ratio, space time). Catalytic results show that the presence of all the elements (Mn, Na<sub>2</sub>WO<sub>4</sub> and SiO<sub>2</sub>) was necessary to obtain optimal performance. The 1.9%Mn-3%Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst exhibited the highest C<sub>2</sub>-yield of 18.5% at a selectivity of 68.6% (Fig. 1a). As-prepared catalysts were amorphous but SiO<sub>2</sub> gradually transformed to cristobalite during exposure to reaction conditions at 810 °C resulting in a strong reduction of the specific surface area (SSA). Both, cristobalite formation as well as SSA reduction had only a marginal influence on catalyst performance (Fig. 1b).



**Fig. 1.** (a) Effect of Mn content in 3%Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> on the OCM reaction, and (b) *In situ* XRD of 1.9%Mn-3%Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalysts at 810 °C with its corresponding C<sub>2</sub>-yield.

[1] T. Ren, M. Patel, K. Blok, *Energy*, **2006**, 31, 425-451.

[2] G.E. Keller, M.M. Bhasin, *J. Catal.*, **1982**, 73, 9-19.

[3] U. Zavyalova, M. Holena, R. Schlögl, M. Baerns, *ChemCatChem*, **2011**, 3, 1935-1947.

[4] J.H. Lunsford, *Catal. Today*, **2000**, 63, 165-174.

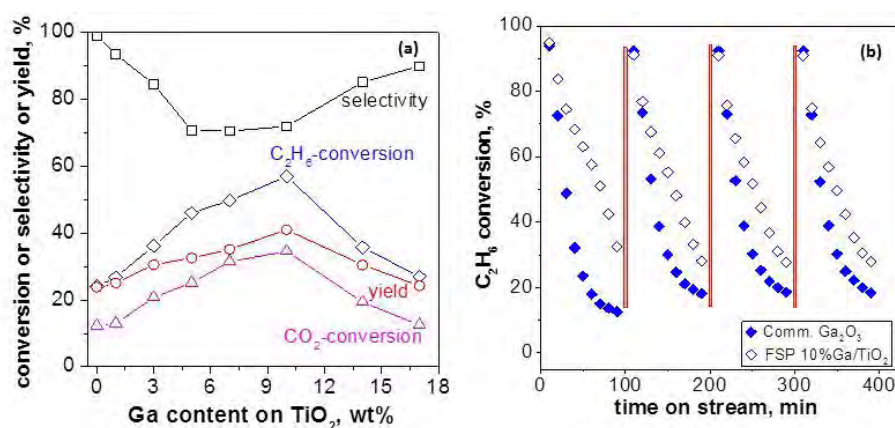
[5] R. Koirala, R. Büchel, S.E. Pratsinis, A. Baiker, *Appl. Catal. A*, **2014** (Submitted)

## Oxidative dehydrogenation of ethane (ODHE) with CO<sub>2</sub> over flame-made Ga-loaded TiO<sub>2</sub>

Rajesh Koirala<sup>1</sup>, Robert Büchel<sup>1</sup>, Sotiris E. Pratsinis<sup>1</sup>, Alfons Baiker<sup>1</sup> \*

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One of the most important feedstocks in chemical industry is ethene, a building block for synthesis of commercially important products, whose demand is increasing with increasing global market [1, 2]. Currently, ethene is produced mostly by steam cracking of naphtha and ethane, which constitute approx. 70% of the production cost while resulting in tons of CO<sub>2</sub> emissions worldwide [3]. The cracking process requires relatively high temperatures (>1000 °C) and severely suffers from coking that forces a complete shutdown of the operation for periodic cleaning [3]. As a consequence, there is a compelling need for the development of an alternative, cost-effective process. Thermal dehydrogenation also suffers from coking, whereas use of O<sub>2</sub> results in lower selectivity. Therefore use of CO<sub>2</sub> as a milder oxidant has been the choice for the ODHE reaction [4].



**Fig. 1.** (a) Effect of Ga loadings on the ODHE reaction at 700 °C, and (b) Regenerability of 10%Ga/TiO<sub>2</sub> in comparison with commercial Ga<sub>2</sub>O<sub>3</sub> in air for 10 min at 700 °C.

The influence of the Ga content (0-17 wt%) in flame-made TiO<sub>2</sub>-supported gallium oxide on the oxidative dehydrogenation of ethane (ODHE) was investigated in a continuous tubular microreactor using CO<sub>2</sub> as oxidant. The ethene yield increased with Ga-loading up to about 10 wt%. Parametric sensitivity studies indicated that the molar CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratio in the feed, temperature and space velocity were decisive parameters for achieving maximum ethene yield. That was 41% using a CO<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratio of 2.5, 700 °C and a space velocity of 6,000 L/kg<sub>cat</sub>·h, corresponding to 57% ethane conversion at 72% selectivity to ethene. Raman spectroscopy of spent catalysts revealed the presence of coke deposition, mainly D and G-type carbon, which led to catalyst deactivation with time-on-stream. However, the catalyst could easily be regenerated with very short oxidation time of 10 min at 700 °C.

[1] C.A. Gartner, A.C. van Veen, J.A. Lercher, *ChemCatChem*, 2013, 5, 3196-3217.

[2] H. Zimmermann, R. Walzl, In *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH Co. KGaA: Weinheim, 2009.

[3] T. Ren, M. Patel, K. Blok, *Energy*, 2006, 31, 425-451.

[4] H.H. Kung, *Adv. Catal.*, 1994, 40, 1-38.

## **In Situ Resonant X-Ray Emission Spectroscopy of Ce<sup>3+</sup> Formation During CO Oxidation at Low Temperatures over Platinum Nanoparticles Supported on Ceria.**

René Kopelent<sup>1</sup>, Szlachetko Jakub<sup>1</sup>, Jeroen A. van Bokhoven<sup>2</sup>, Maarten Nachtegaal<sup>1</sup>, Olga V. Safonova<sup>1</sup> \*

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Platinum nanoparticles supported on ceria shows higher activity for carbon monoxide oxidation at low temperature compared to platinum on inert supports, such as Al<sub>2</sub>O<sub>3</sub>. [1] Whereas on inert supports carbon monoxide and oxygen compete for adsorption sites on platinum, ceria provides active oxygen due to its known oxygen storage capacity (OSC). Ceria can refill oxygen vacancies by oxygen uptake from the gas phase either directly at the interface or neighbouring ceria surface. Platinum nanoparticle provides carbon monoxide adsorbed to its surface and CO oxidation presumably takes place at the Pt-CeO<sub>2</sub> interface. It is assumed that the rate determining step in CO oxidation is the release of oxygen by ceria by generation of Ce<sup>3+</sup> and oxygen vacancies. However, direct spectroscopic evidence is missing.

To gain insight into the reactivity of the ceria substrate we used in situ time-resolved resonant X-ray emission spectroscopy (RXES) on 1.5 wt.% Pt nanoparticles supported on high surface area (75 m<sup>2</sup>/g) ceria present as truncated polyhedra. The sample was excited 5 eV below the Ce L<sub>3</sub> absorption edge at 5.722 keV whereas the X-ray emission spectra were recorded using a von Hamos type spectrometer. To enhance the sensitivity to small spectral variations, we probed the dynamic changes in Ce oxidation state during periodic switches between 1% CO + 4% O<sub>2</sub> vs. 1% CO in Ar gas mixture (total flow 50 ml/min). After initial reduction of the sample in 5% H<sub>2</sub> at 150°C, emission spectra were recorded at temperatures below 50°C and averaged over gas switching cycles. The transient Ce<sup>3+</sup> concentrations were calculated and plotted as a function of gas switch.

After the removal of O<sub>2</sub> the initial rates of Ce<sup>3+</sup> formation agreed within an order of magnitude with steady-state CO conversion rates determined with mass spectrometry. Arrhenius-type plot revealed an activation energy of 44±7 kJ/mol for the reduction of CeO<sub>2</sub>. It agrees well with activation energies measured under steady-state. [2] This is the first spectroscopic evidence that the formation of Ce<sup>3+</sup> at the Pt/CeO<sub>2</sub> interface directly contributes to the rate determining step. The relation with oxygen storage capacity will be discussed.

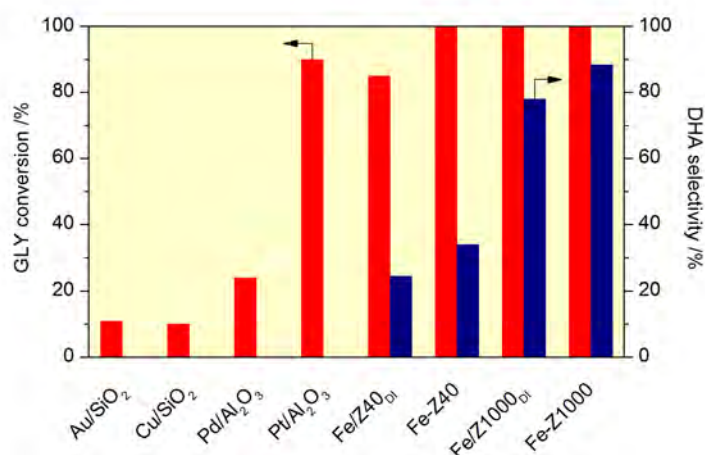
[1] T. Bunluesin, H. Cordatos, R. J. Gorte, *J. Catal.*, **1995**, 157, 222–226.

[2] Matteo Cargnello, Vicky V. T. Doan-Nguyen, Thomas R. Gordon, Rosa E. Diaz, Eric A. Stach, Raymond J. Gorte, Paolo Fornasiero, Christopher B. Murray, *Science*, **2013**, 341, 771–773.



**Gas-phase selective oxidation of glycerol to dihydroxyacetone over iron zeolites**Giacomo Marco Lari<sup>1</sup>, Cecilia Mondelli<sup>1</sup>, Javier Pérez-Ramírez<sup>1</sup> \*<sup>1</sup>ETH Zurich

Dihydroxyacetone (DHA) is a high-value cosmetic additive and an intermediate for the production of lactic acid. The aerobic oxidation of glycerol represents one attractive biobased route to synthesize this chemical. This reaction has been studied in the aqueous phase in the presence of supported noble-metal catalysts, using diluted glycerol solutions and attaining *ca.* 40% DHA yield.<sup>1</sup> Herein, we investigate the oxidation of pure glycerol over Fe-containing MFI-type zeolites in a gas-phase continuous-flow fixed-bed reactor. The metallosilicates are prepared *via* hydrothermal synthesis followed by steaming or *via* dry impregnation (DI) of commercial MFI samples. All catalysts show full conversion and high selectivities (78-88%), the best material being the Al-free hydrothermally-synthesized zeolite. These results greatly contrast the poor activity and selectivity of noble-metal catalysts tested as a reference. UV-Vis, FTIR, and EPR spectroscopy and transmission electron microscopy are applied to characterize the properties of the iron species in the various samples and the acidity of the zeolites<sup>2</sup>. Their outstanding performance, ability to process highly concentrated feeds, and comparably low price make these ferrosilicates appealing for valorization of glycerol to DHA at a large-scale.



**Figure 1.** Glycerol conversion (GLY, red) and DHA selectivity (blue) over metal-containing catalysts.

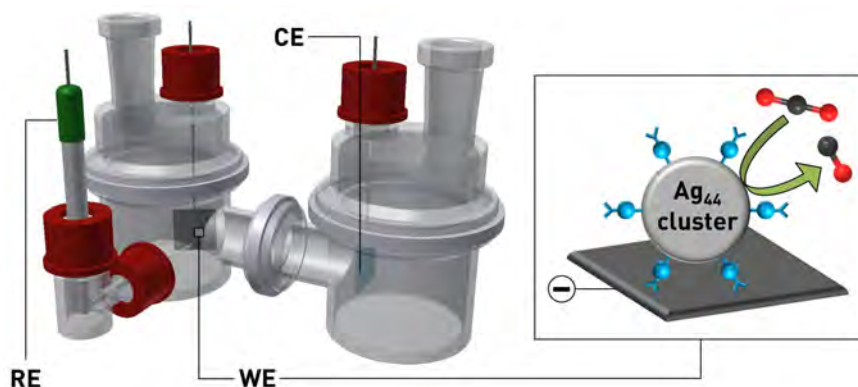
1. H. Kimura, K. Tsuto, T. Wakisaka, Y. Kazumi, Y. Inaya, *Appl. Catal., A* **1993**, 96, 217.
2. A. Ribera, I. Arends, S. de Vries, J. Pérez-Ramírez, R. Sheldon, *J. Catal.* **2000**, 195, 287.

**Electrocatalytic reduction of carbon dioxide by thiol-protected silver nanoclusters**

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The electrochemical conversion of carbon dioxide into fuels and chemicals is one of the most attractive strategies for mitigating CO<sub>2</sub> emissions and avoiding the consequences of climate change, but the practical applicability of this reaction is hampered by the very high overpotential required for the reduction of CO<sub>2</sub>.<sup>1</sup> Thiolate-protected gold nanoclusters have shown remarkable activity in this reaction,<sup>2</sup> highlighting the potential of atomically precise metal nanoparticles to act as efficient electrocatalysts. The alternative use of silver nanoclusters would compare favorably to gold from a cost perspective but has been traditionally limited by their lower stability. Interestingly, a hectogram-scale synthesis of highly stable Ag<sub>44</sub> nanoclusters has been recently reported.<sup>3</sup> In this work, we investigate the electrocatalytic properties of such thiol-protected silver nanoclusters for the reduction of CO<sub>2</sub> to CO.



**Figure 1.** Layout of the two-compartment electrochemical cell employed in this work and schematic representation of the reduction of CO<sub>2</sub> to CO on an Ag<sub>44</sub> nanocluster.

1. E.V. Kondratenko, G. Mul, J. Baltrusaitis, G.O. Larrazábal, J. Pérez-Ramírez, *Energy Environ. Sci.* **2013**, 6, 3112.
2. D.R. Kauffman, D. Alfonso, C. Matranga, H. Qiang, R. Jin, *J. Am. Chem. Soc.* **2012**, 134, 10327.
3. A. Desireddy, B.E. Conn, J. Guo, B. Yoon, R.N. Barnett, B.M. Monahan, K. Kirschbaum, W.P. Griffith, R.L. Whetten, U. Landman, T.P. Bigioni, *Nature* **2013**, 501, 399.



**Rhodium doped ceria: Organics from sunlight, H<sub>2</sub>O and CO<sub>2</sub>?**Fangjian Lin<sup>1</sup>, Ivo Alxneit<sup>1</sup><sup>1</sup>Paul Scherrer Institute, Villigen

The depleting supply of fossil fuels and rapidly increasing emissions of anthropogenic greenhouse gases demand sustainable solutions to the unfolding energy and environmental crises. One very promising route that can contribute is to store solar energy in the form of chemical fuels via thermochemical cycles. Ceria is the state-of-the-art redox materials being studied for solar-driven thermochemical cycles [1]. The syngas produced can be further converted to higher grade fuels such as methane and liquid hydrocarbons. The direct generation of higher grade fuels rather than syngas inherently bypasses the subsequent Fischer-Tropsch process, which could be more economically feasible as it does not require additional storage or transportation of syngas, or Fischer-Tropsch plants. To date, to the best of our knowledge there are no reports in direct generation of organic chemicals from H<sub>2</sub>O and CO<sub>2</sub> by solar thermochemical cycles except a recent work by Cheuh and colleagues [2]. They demonstrated the direct formation of methane from H<sub>2</sub>O and CO<sub>2</sub>, using 10 wt% nickel on samarium-doped ceria. However, H<sub>2</sub> was used to assist the reduction of ceria at much lower temperatures compared to the case of thermal reduction.

Rhodium dispersed on oxide supports has been used to convert syngas to oxygenated liquid fuel such as ethanol. With the aim to generate hydrocarbons such as methane and ethanol directly from H<sub>2</sub>O and CO<sub>2</sub> via thermochemical processes, we incorporated cationic Rh into the ceria lattice by co-precipitation. Conceptually, cationic Rh will play two roles in this system. One is to improve the oxygen storage capacity of ceria, and thus increase fuel production after thermal reduction at a given temperature. The other role is to serve as catalytic sites during the re-oxidation to produce organic chemicals. The formation of organics can be either from the conversion of the syngas generated by H<sub>2</sub>O/CO<sub>2</sub> splitting, or directly from H<sub>2</sub>O/CO<sub>2</sub> without the intermediate formation of syngas, or a combination of both.

X-ray powder diffraction indicates that Rh doped ceria is single-phased. The formation of oxygen vacancies due to the substitution of cerium by the lower valent Rh cations is evidenced by Raman spectra. High temperature X-ray diffraction also reveals that the Rh doped ceria sustains its fluorite structure even at elevated temperatures up to 1400°C, indicating excellent thermal stability highly desired for thermochemical cycles. We also show that Rh doped ceria is very active in the conversion of H<sub>2</sub> and CO<sub>2</sub> into methane, while in the case of native ceria, methane formation is negligible. These demonstrate a great potential of Rh doped ceria for the production of methane and other chemicals during the re-oxidation after thermal reduction, when H<sub>2</sub>O, instead of H<sub>2</sub>, is co-fed with CO<sub>2</sub>. In fact, the re-oxidation of thermally reduced Rh doped ceria by a mixture of gaseous H<sub>2</sub>O and CO<sub>2</sub> shows a very rapid decay of the H<sub>2</sub> signal. The H<sub>2</sub> signal quickly falls back to the background level within half a minute. In comparison, the H<sub>2</sub> signals recorded during the re-oxidation of Zn doped ceria by only H<sub>2</sub>O exhibit a much slower decay. It takes about 10-15 min for the H<sub>2</sub> signal to return to the background level. The decaying rate of the H<sub>2</sub> signals for the Rh doped ceria is 20-30 times that for the Zn doped ceria. This strongly suggests that, in the case of Rh doped ceria, the H<sub>2</sub> produced from the splitting of H<sub>2</sub>O is to certain extent consumed. We believe that this consumption is likely due to CO<sub>2</sub> hydrogenation, and thus the formation of organic molecules seems highly likely.

[1] Chueh, W. C.; Falter, C.; Abbott, M.; Scipio, D.; Furler, P.; Haile, S. M.; Steinfeld, A. *Science* 2010, 330, 1797.

[2] Chueh, W. C.; Haile, S. M. *ChemSusChem* 2009, 2, 735.

**Cobalt-based spinel catalysts for visible-light-driven water oxidation**

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<sup>1</sup>University of Zurich

Artificial photosynthesis for water splitting into H<sub>2</sub> and O<sub>2</sub> is the most promising strategies to address the worldwide demands for clean and sustainable energy.<sup>[1, 2]</sup> Over the past decades, special emphasis has been placed on the water oxidation half reaction which remains the most challenging step of the water splitting process.<sup>[3, 4]</sup> The design of new water oxidation catalysts (WOCs) with low cost and abundant constituents is currently under main focus.

Spinel Co<sub>3</sub>O<sub>4</sub> oxide, due to its low-cost, high activity and sturdy, was considered as one of the most promising WOCs and has been widely studied in the past two decades. However, simultaneous performance optimization of the mixed-valent spinel matrix along with its surface and morphological features remains a major challenge. We herein shed new light on “top down” calcination and “bottom up” hydrothermal strategies to achieve straightforward control over the manifold interdependent design parameters for efficient Co<sub>3</sub>O<sub>4</sub>-WOCs.<sup>[5]</sup>

[1] (a) N. Armaroli, V. Balzani, *Angew. Chem. Int. Ed.* **2007**, 46, 52-66; (b) K. Maeda, *ACS Catal.*, **2013**, 3, 1486-1503; (c) M. Antonietti, *Angew. Chem. Int. Ed.*, **2013**, 52, 1086-1087.

[2] (a) N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA*, **2006**, 103, 15729-15735; (b) Y. Tachibana, L. Vayssieres, J. R. Durrant, *Nat. Photonics*, **2012**, 6, 511-518.

[3] K. J. Young, L. A. Martini, R. L. Milot, R. C. Snoeberger III, V. S. Batista, C. A. Schmuttenmaer, R. H. Crabtree, G. W. Brudvig, *Coord. Chem. Rev.*, **2012**, 256, 2503-2520.

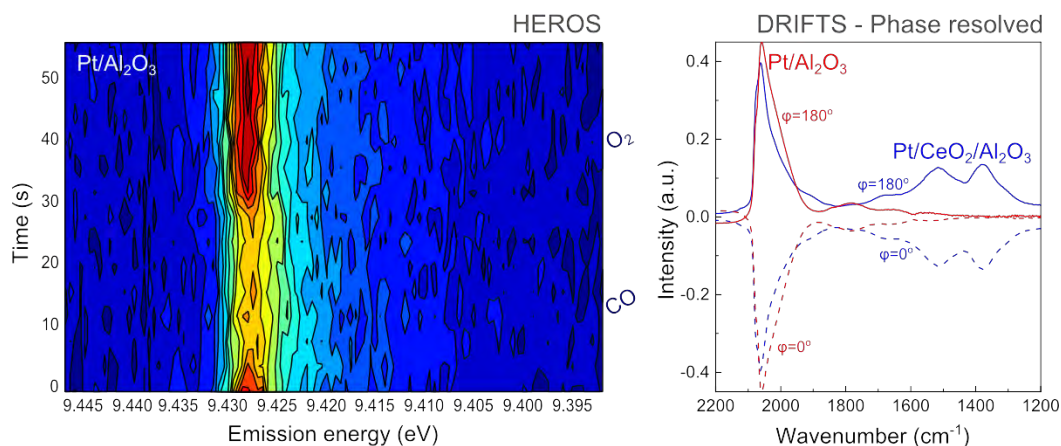
[4] H. Dau, C. Limberg, T. Reier, M. Risch, S. Roggan, P. Strasser, *ChemCatChem*, **2010**, 2, 724-761. [5] H. Liu, G. R. Patzke, *Chem. Asian J.*, **2014**, DOI: 10.1002/asia.201400140

**DRIFTS-HEROS study of CO oxidation on Pt catalysts**

Valentina Marchionni<sup>1</sup>, Szlachetko Jakub<sup>2</sup>, Anastasios Kambolis<sup>1</sup>, Maarten Nachtegaal<sup>1</sup>, Oliver Kröcher<sup>3</sup>, Davide Ferri<sup>1</sup> \*

<sup>1</sup>Paul Scherrer Institute, Villigen, <sup>2</sup>Paul Scherrer Institute, Villigen, <sup>3</sup>Paul Scherrer Institute, Villigen and EPFL Lausanne

The understanding of structure-performance relationships under working conditions is fundamental for catalyst and process development. The combination of complementary spectroscopic techniques in a single experiment is extremely useful to obtain a deeper insight in the catalyst structure under working conditions. Moreover, subjecting the catalyst to fast transient changes is a more suitable approach to selectively access information on active species. In modulation excitation spectroscopy (MES), the catalyst is perturbed by continuous changes of an external parameter with simultaneous acquisition of the spectroscopic signals. To enhance the sensitivity towards structural changes phase sensitive detection (PSD) is applied. MES was used to investigate CO oxidation over Pt-based three way catalysts combining DRIFTS and high energy resolution off-resonant spectroscopy (HEROS)<sup>[1]</sup>. The MES-HEROS study allowed characterizing the dissociative adsorption of oxygen followed by partial oxidation of the Pt subsurface that represent the two stages of the slow oxidation step. PSD facilitated the isolation of faint spectroscopic features of Pt-CO and Pt-O species. We identified an intermediate chemisorbed O on Pt that is adsorbed in atop position. Addition of ceria retards Pt reduction and greatly improves the activity of the catalyst in reducing conditions. DRIFTS data of the same experiment shows different sites for CO adsorption; on Pt/Al<sub>2</sub>O<sub>3</sub> CO is mainly linearly adsorbed on metallic platinum and on weakly coordinated Pt; on Ce-containing sample is more important the contribution of CO adsorbed on Pt atoms with higher coordination degree, furthermore oxidized platinum and small metal particles in strong interaction with the support are observed. In presence of CeO<sub>2</sub> the participation of carbonates to the red-ox process is relevant.



[1] J. Szlachetko, D. Ferri, V. Marchionni, A. Kambolis, O. V. Safonova, C. J. Milne, O. Kröcher, M. Nachtegaal, J. Sá, *J. Am. Chem. Soc.*, **2013**, 135, 19071-19074.

## Operando Monitoring of Surface Processes during Heterogeneous Asymmetric Hydrogenation of Ketones on Chirally-Modified Platinum Catalyst

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Simple addition of trace amounts of cinchonidine (CD) induces remarkably high enantiomeric excess (ee) in the asymmetric hydrogenation of activated ketones on chirally modified platinum (up to 98% ee). Unfortunately, the performance of this catalytic system is highly sensitive to the molecular structures of the ketone and chiral modifier, and even the nature of the solvent and the hydrogen pressure can strongly influence the enantioselection.<sup>[1]</sup> To pave the way towards rational design of such enantioselective catalysts deepening the mechanistic understanding of the stereoselective surface process is indispensable. Up to date, most mechanistic studies of the surface processes relevant to asymmetric hydrogenation on chirally-modified platinum catalysts have been carried out *ex situ*<sup>[2]</sup> or under conditions relatively far from those encountered in practice,<sup>[3]</sup> which imposes some uncertainty about their significance for the mechanistic understanding of these catalytic systems. In this study, the application of operando ATR-IR spectroscopy to uncover the complex surface processes occurring at the catalytic chiral surface of a cinchona-modified Pt catalyst during the asymmetric hydrogenation of activated ketones is presented.<sup>[4]</sup> Achieving essentially the same activity and ee as in a conventional semi-batch reactor, our analytical set-up provides spectroscopic data facilitating a molecular level understanding of the catalytic cycle under realistic working conditions.<sup>[5]</sup> The surface spectra obtained during the asymmetric hydrogenation/deuteration reveal the transient formation of a diastereomeric surface complex involving the chiral modifier, the prochiral ketone and dissociated hydrogen from the catalytic surface. Furthermore, fundamental information about the chiral modification, the influence of the product enantiomers and the role of hydrogen in the catalytic cycle could be gained.

[1] a) T. Mallat, E. Orglmeister, A. Baiker, *Chem. Rev.* **2007**, 107, 4863-4890; b) M. Bartok, *Curr. Org. Chem.* **2006**, 10, 1533-1567; c) F. Zaera, *J. Phys. Chem. C* **2008**, 112, 16196-16203; d) D. Y. Murzin, P. Maki-Arvela, E. Toukoniitty, T. Salmi, *Catal. Rev.-Sci. Eng.* **2005**, 47, 175-256.

[2] V. Demers-Carpentier, G. Goubert, F. Masini, R. Lafleur-Lambert, Y. Dong, S. Lavoie, G. Mahieu, J. Boukouvalas, H. L. Gao, A. H. Rasmussen, L. Ferrighi, Y. X. Pan, B. Hammer, P. H. McBreen, *Science* **2011**, 334, 776-780.

[3] a) D. Ferri, T. Bürgi, *J. Am. Chem. Soc.* **2001**, 123, 12074-12084; b) J. Kubota, F. Zaera, *J. Am. Chem. Soc.* **2001**, 123, 11115-11116.

[4] F. Meemken, K. Hungerbühler, A. Baiker, *Angew. Chem. Int. Ed.* **2014**, DOI: 10.1002/anie.201402981.

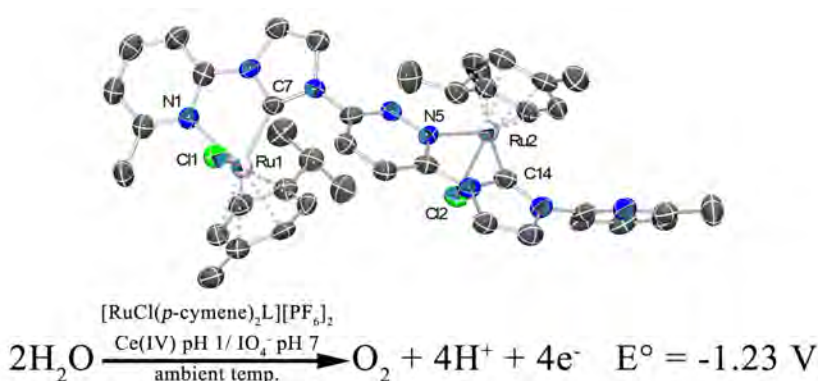
[5] M. A. Banares, *Catal. Today* **2005**, 100, 71-77.

## Engineering Single-Sites Inside Metal Organic Frameworks in the Search for New Water Oxidation Catalysts

Kim Meyer<sup>1</sup>, Jeroen A. van Bokhoven<sup>2</sup> \*

<sup>1</sup>ETH Zurich, <sup>2</sup>ETH Zurich and Paul Scherrer Institute, Villigen

Post-synthetic modification (PSM) of metal organic frameworks (MOFs) is now an established technique for introduction of an array of reactive groups,[1] including amine and amide sites disposed towards coordination of transition metals. Consequently, MOFs are emerging as a promising class of heterogeneous supports for organometallic catalysts.[2] Water Oxidation Catalysis (WOCs) is one particular area in which MOF systems may be exploited. Recent progress in homogeneous WOCs suggests there is a need to develop systems containing single-sites with strong  $\sigma$  and  $\pi$ -donor groups - in conjunction with robust ancillary ligand supports - to increase  $O_2$  TOF and suppress associated catalyst decomposition processes.[3] Cp\*iridium-based WOCs using dibenzoate-substituted 2,2'-bipyridine-type MOFs are among the first forays into this field.[4] A series of novel NHC ( $\sigma$ -donor) and amidate ( $\pi$ -donor) functionalised pyridyl homogeneous ruthenium(II) complexes have been prepared in our laboratory as models for the synthetic strategy required to prepare more complicated MOFs. We disclose the pathways to and properties of these novel materials - including the water oxidation active NHC complexes - and development of NHC, amidate and pyridyl functionalised MOFs. In pursuit of robust MOFs disposed towards WOCs we explore both direct synthesis and PSM techniques for functionalisation of our linkers.



[1] Z. Wang, S. M. Cohen, *Chem. Soc. Rev.*, **2009**, 38, 1315.

[2] J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.*, **2009**, 38, 1450.

[3] L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun, *Nature Chem.*, **2012**, 4, 418; L. Wang, L. Duan, L. Tong, L. Sun, *J. Cat.*, **2013**, 306, 129; R. Staehle, L. Tong, L. Wang, L. Duan, A. Fischer, M. S. G. Ahlquist, L. Sun, S. Rau, *Inorg. Chem.*, **2014**, 53, 1307.

[4] C. Wang, J.-L. Wang, W. Lin, *JACS*, **2012**, 134, 19895.

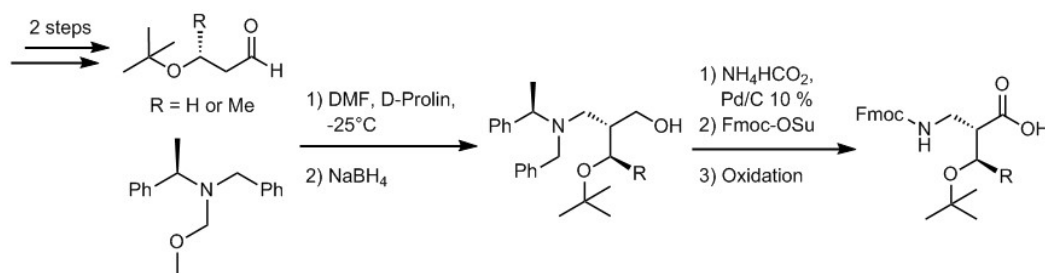
## Scalable Enantioselective Synthesis of Fmoc- $\beta^2$ -Serin and -Threonin by Organocatalytic Mannich Reaction

Daniel Meyer<sup>1</sup>, Dieter Seebach<sup>2</sup>, Roger Marti<sup>1</sup> \*

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Synthesis of  $\beta^2$ -amino acids is still a big challenge and only a few of them are commercially available.[1] In contrast to  $\beta^3$ -amino acids, the  $\beta^2$ -isomers cannot be obtained simply by enantiospecific homologation of the  $\alpha$ -amino acids, but have to be prepared by enantioselective reactions or sequences.  $\beta^2$ -amino acids with functionalized side chains like Fmoc- $\beta^2$ -serin and -threonin requires up to 9 respectively 13 steps from commercially available starting materials.[1]

One possible way to prepare  $\beta^2$ -amino acids is the organocatalytic Mannich reaction.[2][3] This approach was used so far mostly for non-functionalized side chains and on milligram scale.



We report our results on the optimization and scale-up of the organocatalytic Mannich reaction (different catalysts, reaction conditions, substrates) and the synthesis of Fmoc- $\beta^2$ -serin and -threonin on a multi-gram scale in 6 steps starting from commercially available starting materials.

[1] D. Seebach, A. K. Beck, S. Capone, G. Deniau, U. Grošelj, E. Zass, *Synthesis*, **2009**, 1, 1-32.

[2] I. Ibrahem, G.-L. Zhao, A. Cordova, *Chem. Eur. J.*, **2007**, 13, 683-688.

[3] a) Y. Chi, S. H. Gellman, *J. Am. Chem. Soc.*, **2006**, 128, 6804-6805. b) Y. Chi, E. P. English, W. C. Pomerantz, W. S. Horne, L. A. Joyce, L.R. Alexander, W. S. Fleming, E. A. Hopkins, S. H. Gellman, *J. Am. Chem. Soc.*, **2007**, 129, 6050-6055.

**WO<sub>3</sub>-CeO<sub>x</sub>-TiO<sub>2</sub> catalyst prepared by one-step flame spray synthesis for NO<sub>x</sub> reduction in the NH<sub>3</sub>-SCR**

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The current requirements for the control of NO<sub>x</sub> in the exhaust of vehicles and power plants call for catalysts with improved thermal stability. In recent years, cerium oxide has attracted considerable attention due to its oxygen storage capacity and the high redox ability of the Ce<sup>4+</sup>/Ce<sup>3+</sup> pair, and is thus successfully utilized in three way catalysts (TWC) and could be as well applied in the SCR catalyst. A series of WO<sub>3</sub>-CeO<sub>x</sub>-TiO<sub>2</sub> nano-powders with 10 wt% WO<sub>3</sub> and Ce concentration in the range of 0–20 at% were obtained by flame spray synthesis. The structural properties of the materials were characterized by BET, XRD, HRTEM and HAADF STEM. The specific surface area was around 85 m<sup>2</sup>•g<sup>-1</sup> and the TiO<sub>2</sub> particles size of ca. 20 nm. Well crystallized Ti- and Ce-oxide related phases were identified by XRD and confirmed by HRTEM. STEM demonstrated that WO<sub>3</sub> forms an amorphous layer over crystalline phases of Ti- and Ce-oxides. XPS revealed that irrespective of catalyst composition Ti and W were in 4+ and 6+ oxidation states, respectively. Ce was mainly in 3+ oxidation state and the fraction of reduced Ce increased with decreasing concentration of Ce reaching 100% in 10 wt% WO<sub>3</sub>/Ce<sub>0.05</sub>Ti<sub>0.95</sub>O<sub>2</sub>. WO<sub>3</sub> enriched the number and the strength of the acid sites. On the contrary, with increasing Ce content the amount of high temperature acid sites progressively decreased. The WO<sub>3</sub>-CeO<sub>x</sub>-TiO<sub>2</sub> catalysts were tested under NH<sub>3</sub>-SCR conditions in the 150–450°C temperature range. 10 wt% WO<sub>3</sub>/Ce<sub>0.1</sub>Ti<sub>0.9</sub>O<sub>2</sub> showed the best performance, comparable to the well-established V-W-Ti-oxide based SCR catalysts. The excellent performance can be related to the high Ce<sup>3+</sup> content, which is considered the active site in NH<sub>3</sub>-SCR, optimal surface acidity and phase composition.

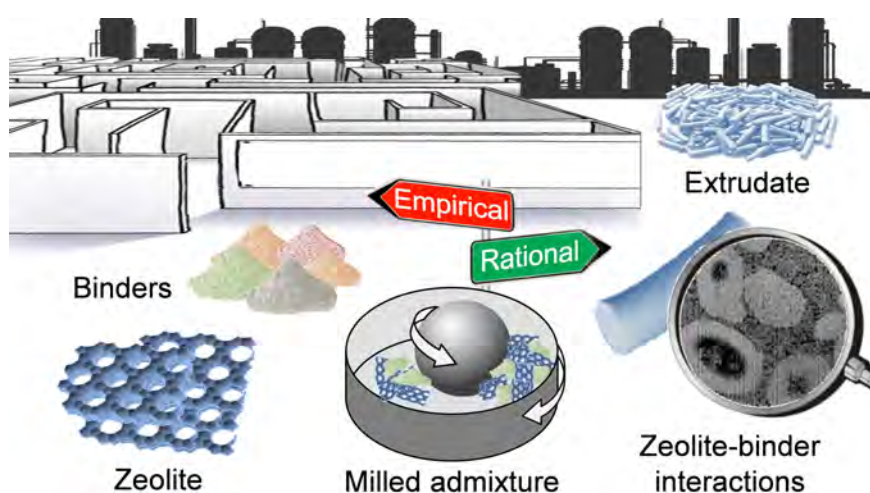


## Effects of binders on the lifetime and selectivity of shaped hierarchical zeolites in MTH

Nina-Luisa Michels<sup>1</sup>, Sharon Mitchell<sup>1</sup>, Javier Pérez-Ramírez<sup>1</sup> \*

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Binders incorporated to improve mechanical stability and related structuring steps can cause decisive performance alterations in technical catalysts, the promoting/inhibiting effects of which are currently difficult to predict.<sup>1</sup> To understand property variations induced by shaping, this contribution focuses on the extrusion of a novel class of hierarchical ZSM-5 zeolite with common silica, boehmite, and clay binders. The cause and extent of binder effects are determined by comparing the properties and methanol-to-hydrocarbons (MTH) performance of the extrudates with respect to appropriate reference samples. The findings demonstrate that the development of auxiliary mesopores must be coupled with the correct choice of binder to maximize the catalyst lifetime. Ball milling is an effective technique to detect interactions responsible for the significant lifetime variations observed. The important role of mobile ions in promoting the longevity and light olefin selectivity of attapulgite-containing extrudates is demonstrated. An improved understanding of the evolution of zeolite-binder mixtures during structuring will accelerate the development of superior catalytic technologies.



**Figure 1.** Rational design of shaped zeolite catalysts for the valorization of methanol.

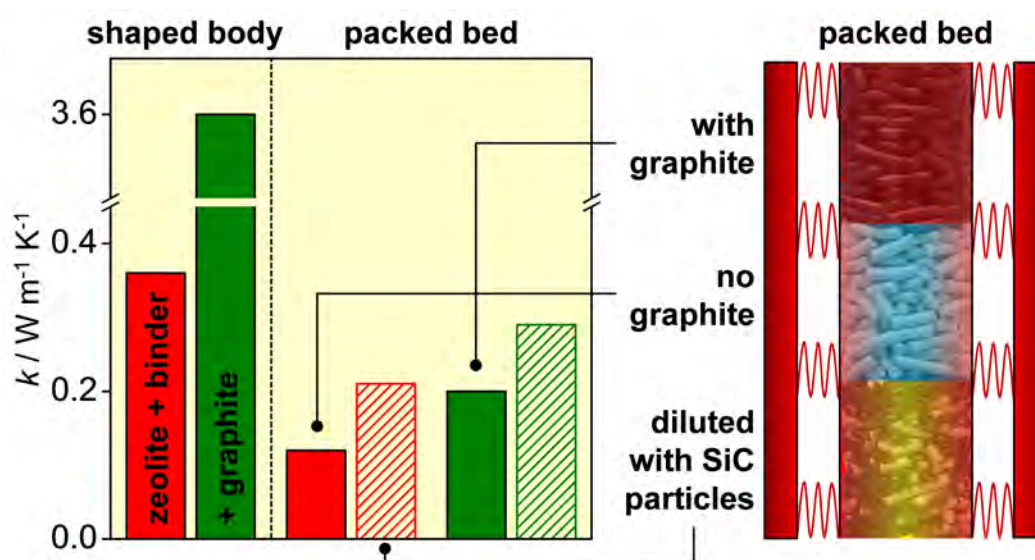
1. S. Mitchell, N.-L. Michels, J. Pérez-Ramírez, *Chem. Soc. Rev.* **2013**, 42, 6094.

## Technical catalyst design: effective application of additives to enhance thermal conductivity

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Despite regulating the heat transfer in heterogeneously-catalyzed processes, thermal conductivity is rarely considered in the academic design of catalysts.<sup>1</sup> For insulating materials such as zeolites, various thermally-conductive agents could be incorporated to enhance the intrinsic thermophysical properties,<sup>2,3</sup> yet few guidelines exist with regard to how this can be effectively accomplished. Herein, we study the impact of copper, silicon carbide, or graphite on the thermal conductivity of individual pellets and extrudate beds of ZSM-5 zeolites. In a single pellet, the type, amount, and interconnectivity of the additive and the pore volume of the body are found to be highly influential. The enhancements achieved over the individual bodies can be extrapolated to the catalyst bed, although the overall thermal conductivity is significantly reduced due to the larger void volume. Bed dilution, for example with silicon carbide, is shown to be comparable and additive effect to those of introducing an internal additive (Fig. 1). Finally, the temperature dependency of the catalyst thermal conductivity and the impact in catalysis is assessed.



**Figure 1.** Rationalizing the importance of thermal conductivity in catalyst design.

1. S. Mitchell, N.-L. Michels, J. Pérez-Ramírez, *Chem. Soc. Rev.* **2013**, 42, 6094.
2. D.S. Smith, A. Alzina, J. Bourret, B. Nait-Ali, F. Pennec, N. Tessier-Doyen, K. Otsu, H. Matsubara, P. Elser, U.T. Gonzenbach, *J. Mater. Res.* **2013**, 28, 2260.
3. Y. Liu, O. Ersen, C. Meny, F. Luck, C. Pham-Huu, *ChemSusChem* **2014**, 7, 1.

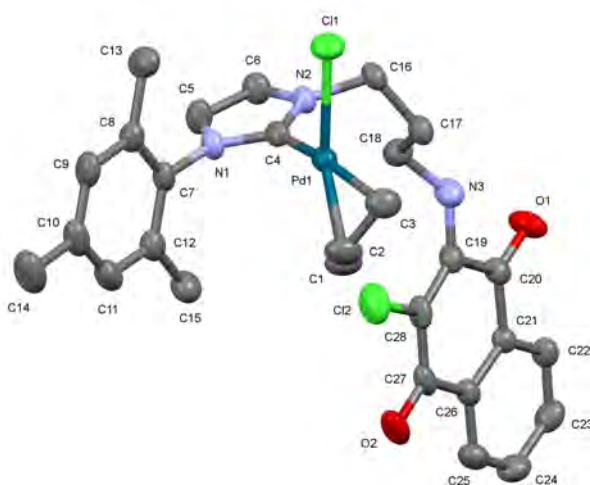
**Metal Complexes with N-Heterocyclic Carbenes Bearing Redox Active Groups**

Ewa Milopolska<sup>1</sup>, Markus Neuburger<sup>1</sup>, Thomas R. Ward<sup>2</sup> \*

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In order to address some of the society's grand challenges, chemists must master catalytic reactions relying on multi-electron processes. In this context, redox active ligands offer an attractive means to tune the reactivity of transition metal complexes.[1]

Thanks to its versatility in stabilizing transition metals in various oxidation states, we have selected the *N*-heterocyclic carbene as a scaffold, to which we append a variety of redox active moieties. We present preliminary results summarizing our efforts in synthesizing and studying the coordination- and redox properties of such *N*-heterocyclic carbenes with a variety of transition metal complexes.



[1]. P.Vijayendran, M. R. Ringenberg, T. R. Ward, *Angew. Chem. Int. Ed.*, 2012, 51 , 10228.

## **Coupling of hydrogen and oxygen evolution electrocatalysts to photoelectrodes for the production of solar fuels.**

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The efficient and inexpensive storage of solar energy in the form of chemical bonds is one of the most promising solutions towards the continuous supply of electricity and carbon-neutral fuels to cities and industries. Solar irradiation reaching the surface of the Earth in a period of one hour alone could be enough to satisfy our energy demands for one whole year at current consumption rates. Metal oxide photoelectrodes with small band gap (Photoelectrochemical (PEC) tandem cells have been predicted to reach over 25% solar-to-hydrogen (STH) conversion efficiencies even when realistic energy losses are taken into account,<sup>[1]</sup> and monolithic PEC cells with an integrated photovoltaic device have already been shown to split water upon illumination with over 12% STH efficiency.<sup>[2]</sup> However, these devices are made of materials that are prohibitively expensive for large scale practical applications, and thus, attention has shifted towards the realization of devices that are both efficient and cost-effective during the last decades.

Just as in electrolyzers, a PEC water splitting device requires efficient electrocatalysts for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). In addition to high electrochemical performance and stability, electrocatalyst for PEC water splitting need to be optically transparent to allow illumination of the top and bottom photoelectrodes in a tandem device and form a stable electrical contact with the underlying photoabsorbing material. We have recently reported an amorphous molybdenum sulfide HER catalyst that can be coupled to a copper (I) oxide photocathode to achieve stable photocurrents of up to  $-5.7 \text{ mA cm}^{-2}$  at 0 V vs the reversible hydrogen electrode. In the same manner, we have recently developed a simple and versatile deposition method for various optically transparent Earth-abundant OER catalyst onto metal oxide photoanodes. Deposition of OER catalyst improve the onset potential by close to 300mV and the photocurrents obtained in a tandem cell for un-assisted water splitting are among the highest reported for metal oxide photoanodes and devices made entirely of abundant elements.

[1] Shu Hu, Chengxiang Xiang, Sophia Haussener, Alan D. Berger, Nathan S. Lewis, *Energy Environ. Sci.*, **2013**, 6, 2984-2993.

[2] Jan Rongé, Tom Bosserez, David Martel, Carlo Nervi, Luca Boarino, Francis Taulelle, Gero Decher, Silvia Bordigac, Johan A. Martens, *Chem. Soc. Rev.*, **2014**, DOI: 10.1039/c3cs60424.

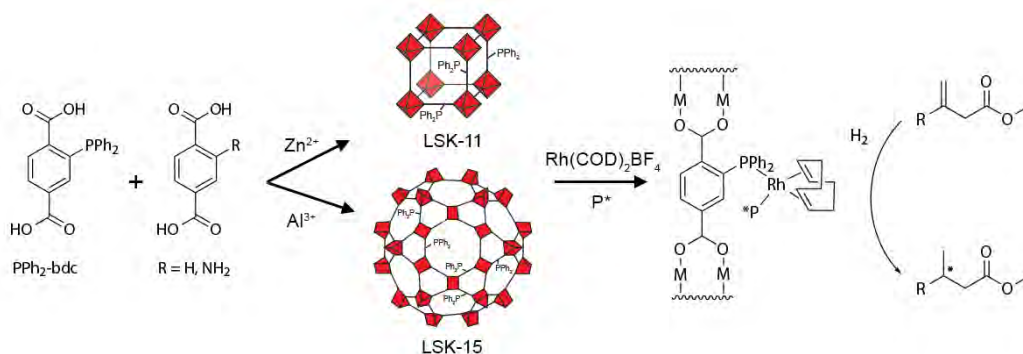
[3] Carlos G. Morales-Guio, S. David Tilley, Heron Vrubel, Michael Grätzel, Xile Hu, *Nat. Commun.*, **2014**, 5, 3059

## Towards heterogeneous asymmetric hydrogenation of olefins using phosphine-substituted metal-organic frameworks

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<sup>1</sup>ETH Zurich, <sup>2</sup>Paul Scherrer Institute, Villigen, <sup>3</sup>ETH Zurich and Paul Scherrer Institute, Villigen

Metal-organic frameworks (MOFs) are nanoporous coordination polymers, which attract great interest due to their potential applications in gas sorption, biomedical application and catalysis.[1] Their well-defined structures and flexibility toward the incorporation of chemical functional groups make MOFs ideal candidates for metal-supported catalysis.[2]



Here, we present a series of novel phosphine-functionalized MOFs based on a substituted terephthalic acid (PPh<sub>2</sub>-bdc).[3] We will demonstrate how NMR and XAS can be used to characterize the phosphorus functional groups. We will also illustrate that these structures act as support for organometallic complexes and can be applied for Rh-catalyzed asymmetric hydrogenation of olefins.

[1] J. Rowsell, O. M. Yaghi, *Microporous Mesoporous Mater.* **2004**, 73, 3–14.

[2] J. Václavík, M. Servalli, C. Lothschütz, J. Szlachetko, M. Ranocchiari, J.A. van Bokhoven, *ChemCatChem* **2013**, 5, 692–696.

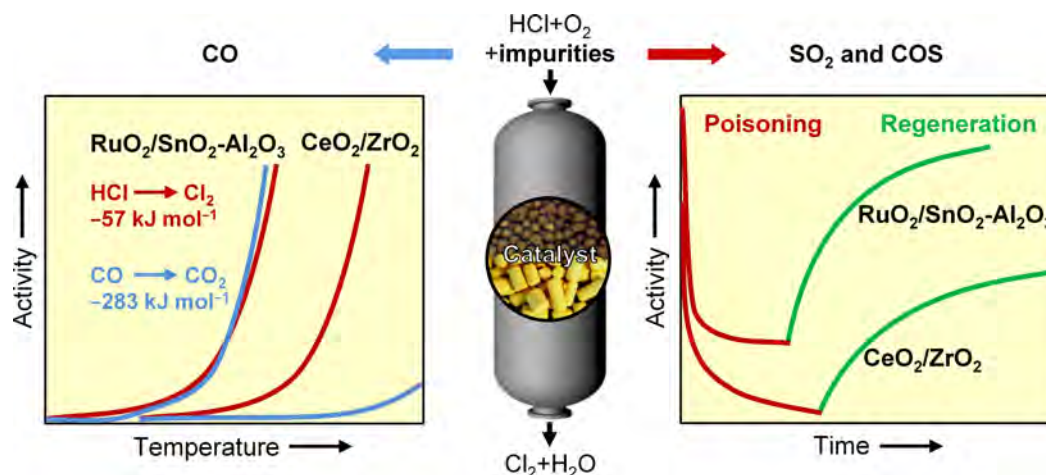
[3] F. L. Morel, M. Ranocchiari, J.A. van Bokhoven, *Ind. Eng. Chem. Res.* **2014**, in press

## Impact of feed impurities on catalyst design for chlorine recycling

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<sup>1</sup>ETH Zurich

The catalyzed oxidation of HCl to Cl<sub>2</sub> comprises a sustainable route to recycle chlorine in the chemical industry.<sup>1</sup> Herein, we shed light onto the impact of impurities typically present in technical HCl streams, *i.e.* carbon monoxide and sulfur compounds, on the catalyst performance. Under reaction conditions, the oxidation of CO to CO<sub>2</sub> over RuO<sub>2</sub>/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and IrO<sub>2</sub>/TiO<sub>2</sub> leads to a significant temperature rise in the catalyst bed. The latter increases the risk of hot spot formation in large-scale reactors, which undermines a stable and safe catalyst operation. In the case of CeO<sub>2</sub>/ZrO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>/ZrO<sub>2</sub>, and CuCrO<sub>2</sub>, CO oxidation is marginal due to a more extensive chlorination of the surface and subsurface of the active phases. The presence of COS and SO<sub>2</sub> in the feed induces a strong deactivation of all catalysts investigated due to poisoning by sulfur compounds. Their activity can be restored by an HCl treatment at the reaction temperature, as demonstrated for RuO<sub>2</sub>/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>/ZrO<sub>2</sub>. The insensitivity of HCl oxidation catalysts like CeO<sub>2</sub>/ZrO<sub>2</sub> towards CO paves the way for an improved process design, in which sulfur and CO removal steps can be separated.



**Figure 1.** Catalytic HCl oxidation in the presence of feed impurities.

1. J. Pérez-Ramírez, C. Mondelli, T. Schmidt, O.F.-K. Schlüter, A. Wolf, L. Mleczko, T. Dreier, *Energy Environ. Sci.* **2011**, 4, 4786.



## A Novel Non-hydrolytic Sol-gel Route to Blue Tungsten Oxide and its Electrochemical Stability

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<sup>1</sup>ETH Zurich, <sup>2</sup>Paul Scherrer Institute, Villigen

Polymer Electrolyte Fuel Cells (PEFCs) are promising alternatives to many fossil fuel based power generators, however the wider use of PEFCs is currently limited by their short operation lifetimes due to catalyst layer degradation. Therefore much research is being directed towards the development of more stable catalyst supports, mainly metal oxide based. Here we report the synthesis of tungsten oxide using non-hydrolytic sol-gel chemistry. Reaction of  $\text{WCl}_6$  or  $\text{WCl}_4\cdot\text{dme}$  with diisopropyl ether in 1,2-dichloroethane yields sub-stoichiometric tungsten oxide ( $\text{WO}_{3-x}$ ) with high surface area. These materials are characterised using TEM,  $\text{N}_2$  adsorption-desorption, XRD, UV-visible spectroscopy and EPR spectroscopy. TEM and XRD characterisation reveals the contrasting morphology and crystallinity of  $\text{WO}_{3-x}$  prepared from these precursors. Interestingly, as-prepared materials are high surface area and have good electron conductivity values ( $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ ), which can be increased with high temperature  $\text{N}_2$  treatment. Analogous treatment under airflow leads to a decrease in conductivity likely due to the filling of oxygen defects. The electrochemical stability of these materials is currently under investigation.

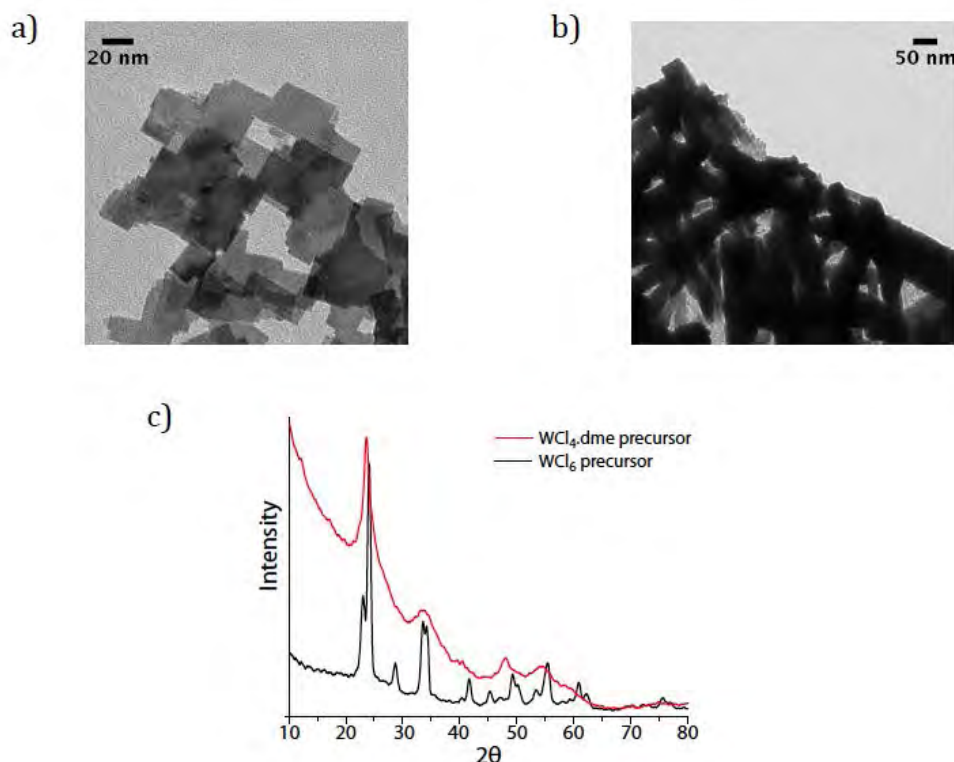


Figure 1: TEM images of  $\text{WO}_{3-x}$  prepared from a)  $\text{WCl}_6$  and b)  $\text{WCl}_4\cdot\text{dme}$  and c) XRD diffraction patterns of  $\text{WO}_{3-x}$  prepared from  $\text{WCl}_6$  and  $\text{WCl}_4\cdot\text{dme}$

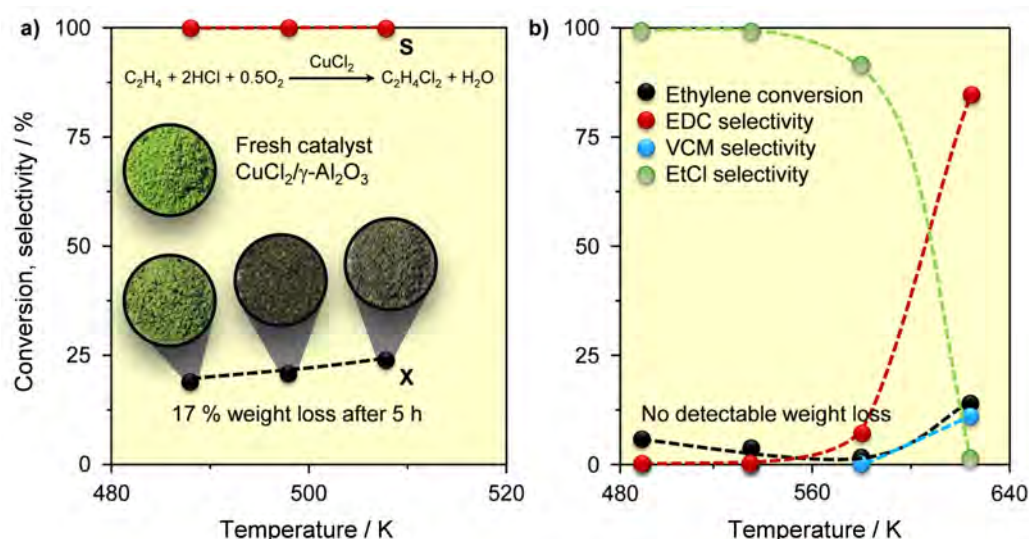


## Is a good Deacon catalyst a good oxychlorination catalyst?

Vladimir Paunovic<sup>1</sup>, Julian Straus<sup>1</sup>, Maximilian Moser<sup>1</sup>, Izabela Czekaj<sup>1</sup>, Javier Pérez-Ramírez<sup>1</sup> \*

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The oxychlorination of ethylene to ethylene dichloride (EDC), a key intermediate in the production of polyvinyl chloride (PVC), is one of the most important processes in today's polymer industry.<sup>1</sup> Promoted  $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$  catalysts, originally designed for HCl oxidation (Deacon reaction), have exclusively been applied to this reaction in both fixed- and fluidized-bed reactor configurations. However, as these materials suffer from severe deactivation due to active phase loss by volatilization and to particle agglomeration, the development of more robust catalysts would translate into a tremendous benefit for the PVC manufacturing industry. With this aim, we unraveled the deactivation mechanism of copper-based systems and evaluated the ethylene oxychlorination performance of new generation Deacon materials, *i.e.*  $\text{RuO}_2$  and  $\text{CeO}_2$ -based systems (Fig. 1).<sup>2</sup> By means of catalyst characterization and Density Functional Theory (DFT) studies, a molecular-level understanding of their chemistry was gathered.



**Figure 1.** Ethylene oxychlorination over a) the state-of-the-art  $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$  and b)  $\text{CeO}_2/\text{ZrO}_2$  catalysts.

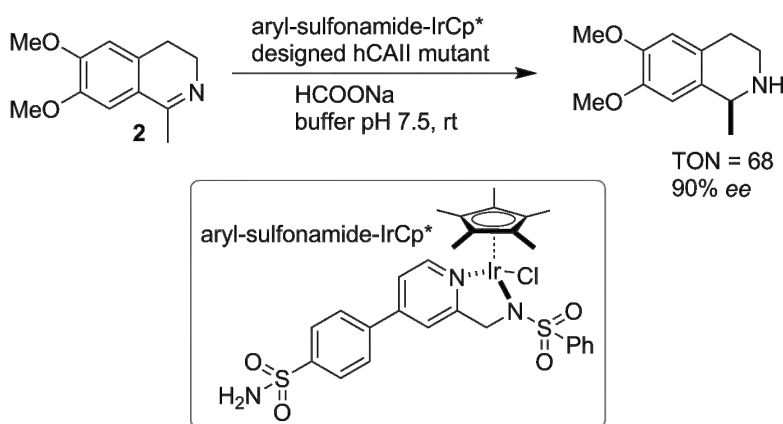
1. J.S. Naworski, E.S. Velez, *Applied Industrial Catalysis 1*, Academic Press, New York, **1983**, 239.
2. J. Pérez-Ramírez, C. Mondelli, T. Schmidt, O.F.-K. Schlüter, A. Wolf, L. Mleczko, T. Dreier, *Energy Environ. Sci.* **2011**, 4, 4786.

## Catalytic Performance of Artificial Imine Reductases Based on Designed Variants of hCAII

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<sup>1</sup>University of Milan, <sup>2</sup>University of Basel, <sup>3</sup>University of Washington

It has been shown in a previous study that the incorporation of IrCp\* complex **1** into human carbonic anhydrase II (hCAII) isoforms leads to active and selective hybrid catalysts for the asymmetric transfer hydrogenation of imine **2** (TON = 47, 70 % ee). Particularly noteworthy was the apparent protein acceleration observed upon binding of the iridium-cofactor to hCAII.<sup>1</sup> Here we report on the catalytic performance of hCAII mutants designed for improved affinity with the Rosetta-design suite.<sup>2</sup> The *in silico* screening identified 8 beneficial mutations which were targeted to afford a total of 50 hCAII mutants.



[1] F. W. Monnard, E. S. Nogueira, T. Heinisch, T. Schirmer, T. R. Ward, *Chem. Sci* **2013**, 4, 3269-3274.

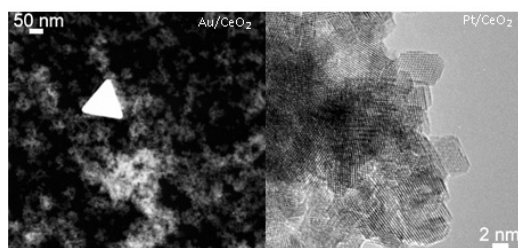
[2] C. E. Tinberg, S. D. Khare, J. Dou, L. Doyle, J. Nelson, A. Schena, W. Jankowski, C. G. Kalodimos, K. Johnsson, B. L. Stoddard, D. Baker, *Nature* **2013**, 501, 212-216.

## One-pot polyol synthesis of Pt/CeO<sub>2</sub> and Au/CeO<sub>2</sub> nanopowders as catalysts for CO oxidation

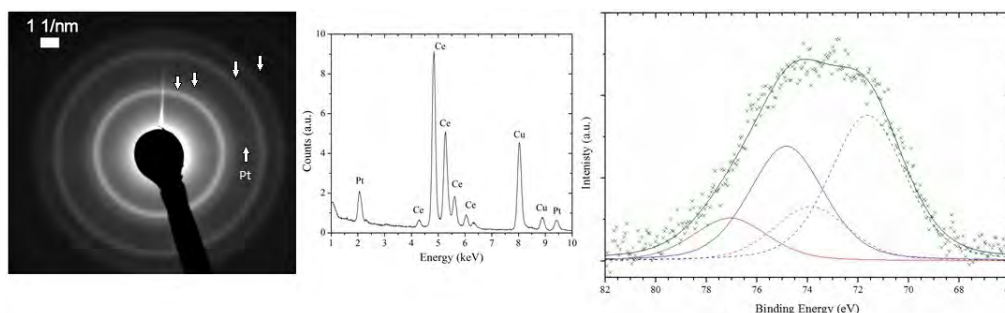
Frank Pilger<sup>1</sup>, Andrea Testino<sup>2</sup>, Christian Ludwig<sup>1</sup> \*

<sup>1</sup>EPFL Lausanne, <sup>2</sup>Paul Scherrer Institute, Villigen

The facile one-pot synthesis of CeO<sub>2</sub>-based catalysts has been developed to prepare a relatively large amount of nanopowders with relevant catalytic activity towards CO oxidation. Two catalysts were prepared: Pt/CeO<sub>2</sub> and Au/CeO<sub>2</sub>. In spite of the identical preparation protocol, Au and Pt behave in a completely different way: Au forms rather large particles, most of them with triangular shape, easily identifiable and dispersed in the CeO<sub>2</sub> matrix. In contrast, Pt was not identified as isolated particles [1]. This is depicted in the HAADF-STEM image (left) and the HRTEM image (right), respectively.



The high resolution X-ray diffraction carried out on the Pt/CeO<sub>2</sub> thermally treated sample (500 °C for 1 h) shows a significant CeO<sub>2</sub> lattice shrinkage, which can be interpreted as an at least partial incorporation of Pt into the CeO<sub>2</sub> crystal lattice, which is supported by first-principle calculations [2] and experimentally demonstrated only by combustion synthesis methods [3]. Moreover, no evidence of metallic Pt was found in both XRD and electron diffraction patterns (bottom left), whereas the energy dispersive X-ray spectra proves the opposite (center). Only Pt<sup>2+</sup> and Pt<sup>4+</sup> species were identified by XPS (bottom right). To the best of our knowledge, this is the first report where ionically dispersed Pt into the CeO<sub>2</sub> lattice is obtained via a liquid synthesis method. The thermally treated Pt/CeO<sub>2</sub> sample revealed good activity with 50% CO conversion at almost room temperature.



[1] Frank Pilger, Andrea Testino, Mattia A. Lucchini, Anastasios Kambolis, Mohamed Tarik, Maria El Kazzi, Yadira Arroyo, Marta D. Rossell, Christian Ludwig, *Journal of Nanoscience and Nanotechnology*, in press.

[2] Bhaskar D. Mukri, Umesh V. Waghmare, M.S. Hedge, *Chemistry of Materials*, **2013**, 25 (19), 3822-3833.

[3] Parthasarathi Bera, K.C. Patil, V. Jayaram, G.N. Subbanna, M.S. Hedge, *Journal of Catalysis*, **2000**, 196, 293-301.

## Towards in situ photoelectron spectroscopy on different formic acid decomposition catalysts

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Formic acid is an attractive hydrogen storage medium. Essential is the selective decomposition into hydrogen and carbon dioxide, which requires the development of an active and selective catalyst. Different materials for formic acid decomposition have been studied [1-5] and different catalyst-adsorbate structures have been proposed. To determine the structure of the catalyst and the adsorbate, photoelectron spectroscopy has been applied [1-3]. Photoelectron spectroscopy yields the structure of the catalyst [1,2] and that of adsorbed species[3].

Most characterization is applied on catalysts with pre-adsorbed formic acid and not under catalytic working conditions. The information about the actual structure of the catalyst and the adsorbates during the decomposition process is therefore not known. In our lab, gold nanoparticles on different metal oxide supports, such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CeO<sub>2</sub>, TiO<sub>2</sub> and ZnO, have been studied during formic acid decomposition with analysis of the decomposition products by mass spectrometry and gas chromatography, providing an excellent basis for comparison to literature and in situ XPS data. The comparison of the selectivity and activity of the different catalysts shows the importance of the interaction of the gold particles with the support, with Al<sub>2</sub>O<sub>3</sub> being superior regarding activity and selectivity to the other support materials.

To find reaction conditions for which in situ photoelectron spectroscopy will provide unique input, decomposition experiments in a low pressure setup are performed. A setup for in situ photoelectron spectroscopy is described, being attached to the spectrometer described in detail in this paper [7], operating in the temperature range from RT to 300°C at pressures below one mbar with formic acid dosing from an evaporator without carrier gas.

[1] D. A. Bulushev, S. Beloshapkin, P. E. Plyusnin, Y. V. Shubin, V. I. Bukhtiyarov, S. V. Korenev, J. R. H. Ross, *J. Catal.* **2013**, 299, 171-180.

[2] A. Ciftci, D. A. J. M. Ligthart, P. Pastorino, E. J. M. Hensen, *Appl. Catal. B Environ.* **2013**, 130-131, 325-335.

[3] Y. Lykhach, M. Happel, V. Johánek, T. Skála, F. Kollhoff, N. Tsud, F. Dvořák, K. C. Prince, V. Matolín, J. Libuda, *J. Phys. Chem. C* **2013**, 117, 12483-12494.

[4] A. Gazsi, G. Schubert, P. Pusztai, F. Solymosi, *Int. J. Hydrog. Energy* **2013**, 38, 7756-7766.

[5] M. Xu, H. Noei, M. Buchholz, M. Muhler, C. Wöll, Y. Wang, *Catal. Today* **2012**, 182, 12-15.

[6] A. Cuesta, G. Cabello, F. W. Hartl, M. Escudero-Escribano, C. Vaz-Domínguez, L. A. Kibler, M. Osawa, C. Gutiérrez, *Catal. Today* **2013**, 202, 79-86.

[7] M. A. Brown, A. B. Redondo, I. Jordan, N. Duyckaerts, M.-T. Lee, M. Ammann, F. Nolting, A. Kleibert, T. Huthwelker, J.-P. Mächler, M. Birrer, J. Honegger, R. Wetter, H. J. Wörner, J. A. van Bokhoven, *Rev. Sci. Instrum.* **2013**, 84, 073904-073904-8.

**Oxygen Reduction on Pt/SnO<sub>2</sub> Catalysts: a Model Electrode Study**

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Polymer electrolyte fuel cells (PEFCs) are, among other applications, an attractive alternative to combustion engines or batteries as power unit for future low or zero emission vehicles. However, for a large market penetration the overall long-term performance of the PEFC needs to be improved. A major part of the efficiency losses is caused by the degradation of the catalyst support of the oxygen electrode leading to a loss of the noble metal catalyst. To improve the durability of the catalyst support and thus the catalyst, metal oxides have been exploited as support material providing significantly higher thermodynamic stability than commonly used carbon blacks [1]. Some investigations showed improved durability of SnO<sub>2</sub> supported Pt-based electrocatalysts [2], but there are still open questions regarding the reaction mechanism of the oxygen reduction reaction (ORR) of SnO<sub>2</sub> supported Pt such as possible metal-support interactions.

In this contribution, we developed model electrodes based on SnO<sub>2</sub> thin films deposited by reactive magnetron sputtering, which have been catalyzed with Pt nanoparticles. By producing SnO<sub>2</sub> films with different crystal orientations the effect of the support surface on the ORR activity of the catalysts could be examined [3]. Further, varying the Pt loading allowed the study of the ORR on different Pt structures, from single particles via agglomerates up to thin films.

[1] Annett Rabis, Paramaconi Rodriguez, Thomas J. Schmidt, *ACS Catalysis*, **2012**, 2, 864.

[2] Fumiaki Takasaki, S. Matsuie, Yoshitsugu Takabatake, Zhiyun Noda, Atsushi Hayashi, Yusuke Shiratori, Kohei Ito and Kazunari Sasaki, *Journal of The Electrochemical Society*, **2011**, 158, B1270.

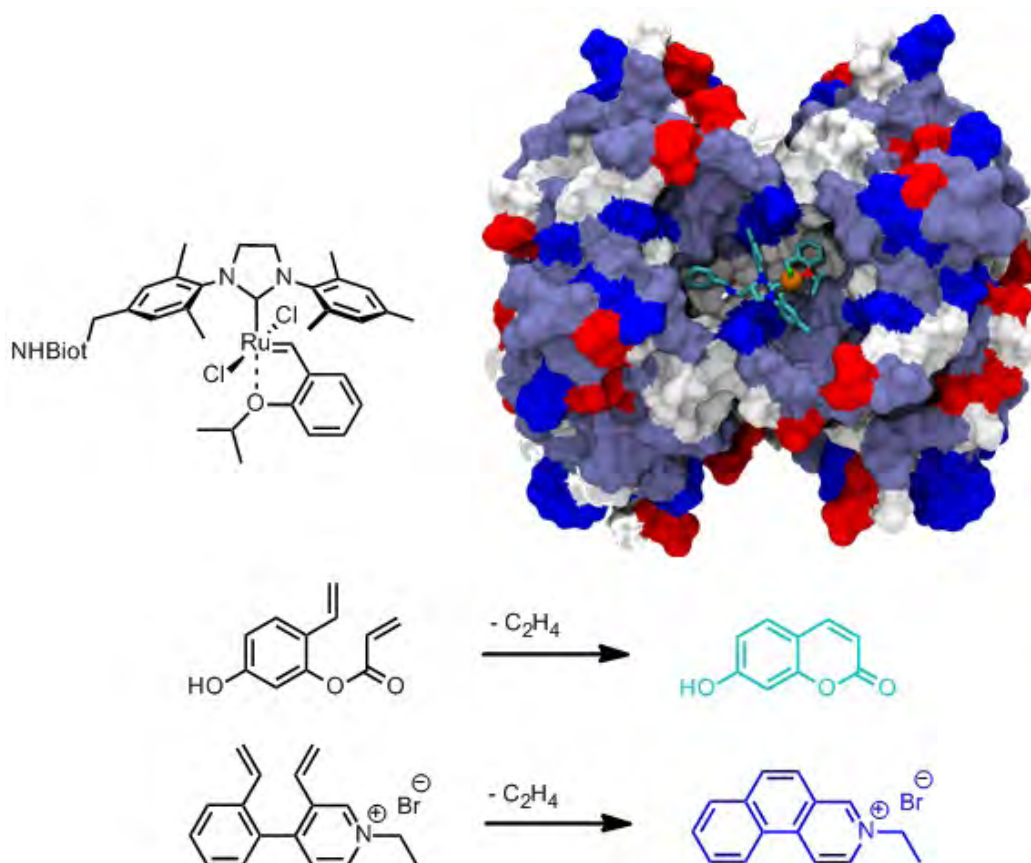
[3] Annett Rabis, Denis Kramer, Emiliana Fabbri, Matt Worsdale, Rüdiger Kötz, Thomas J. Schmidt, *Journal of Physical Chemistry C*, **2014**, doi: 10.1021/jp4120139.

## Development of artificial Metalloenzymes for Ring closing Metathesis based on the Biotin-(Strept)avidin Technology

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<sup>1</sup>University of Basel

Artificial metalloenzymes are constructs consisting of a synthetic catalyst anchored to a protein environment. Such artificial enzymes hold the potential to combine beneficial aspects of biocatalysts with the variety of chemical transformations achieved by transition metal catalysts.[1] One example of a reaction which cannot be catalyzed by natural enzymes but is of mayor interest in research as well as in industry is olefin metathesis. Exploiting the biotin-(strept)avidin technology, different biotinylated Hoveda-Grubbs 2<sup>nd</sup> generation type catalysts have been prepared and combined with streptavidin mutants.[2,3] To enable a rapid screening of streptavidin mutant libraries, a reaction setup was developed which will allow for rapid analysis of large protein libraries by employing substrates which produce fluorescent products upon ring closing metathesis.



[1] T. R. Ward, *Acc. Chem. Res.* **2011**, 44, 47.

[2] C. Lo, M. R. Ringenberg, D. Gnadet, Y. Wilson, T. R. Ward, *Chem. Commun.* **2011**, 47, 12065.

[3] A. Kajetanowicz, A. Chatterjee, R. Reuter, T. R. Ward, *Catal. Lett.* **2014**, 144, 373.

**Extent-based Model Identification of Surface Catalytic Reaction Systems**

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<sup>1</sup>EPFL Lausanne

Identification of kinetic models and estimation of reaction and mass-transfer parameters is an important task for monitoring, control and optimization of industrial processes. A methodology called Extent-based Model Identification has been developed to separate the effects of reaction, mass transfer, and inlet and outlet flows for homogeneous and gas-liquid reaction systems. The decoupled effects, called extents, are used to decompose the model identification task incrementally into sub-problems of lower complexity, in which measured data are first transformed into extents and these extents are then modeled individually [1-3].

For the analysis of surface catalytic reaction systems, it is important to separate the coupled effects of transport phenomena and reactions. Therefore, the methodology of Extent-based Model Identification has been extended to gas-solid and gas-liquid-solid systems involving catalytic processes at the surface of a solid catalyst, described by Langmuir-Hinshelwood types of kinetic models.

From measurements in the fluid and solid phases, the extent of each individual dynamic process is computed. A model is postulated for that process and the corresponding extent is simulated and compared with the computed extent. This procedure allows performing model identification and parameter estimation individually for each phenomenon and species (diffusion of substrates and products, adsorption of substrates, desorption of products and solid-phase reactions).

[1] Bhatt et al., *Ind. Eng. Chem. Res.*, **2011**, 50, 12960-12974

[2] Srinivasan et al., *Chem. Eng. J.*, **2012**, 208, 785-793

[3] Billeter et al., *Anal. Chim. Acta*, **2013**, 767, 21-34



**Reactivity of Active Sites on gamma-Alumina: Towards C-C Bond Formation**

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<sup>1</sup>ETH Zurich, <sup>2</sup>ENS Lyon

Transition aluminas are widely used as catalysts or catalyst supports in heterogeneous catalysis. These transition aluminas exhibit Al-III sites which can activate numerous molecules, including H<sub>2</sub> and alkanes. We have recently shown that H-X (X = H and CH<sub>3</sub>) are activated on Al-O sites via an heterosplitting of the H-X bond. [1]

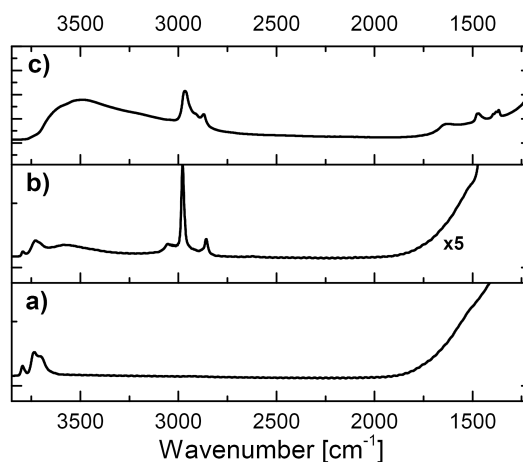


Figure 1: gamma-Alumina pretreated under high-vacuum at 700 °C (**a**), contacted with CH<sub>3</sub>F at room temperature (**b**), after 1 hr after contact at room temperature (**c**).

Here we discuss the reactivity of these sites towards halogenated hydrocarbons (RCH<sub>2</sub>X, with X = F and Cl, R = CH<sub>3</sub> or CH<sub>2</sub>CH<sub>3</sub>) through a combined experimental and computational approach, and demonstrate the formation of C-C bonds.

[1] Wischert *et al.* *Angew. Chem. Int. Ed.* **2011**, 50, 3202. Rascón *et al.*, *Chem. Sci.* **2012**, 2, 1449. Wischert *et al.*, *J. Am. Chem. Soc.*, **2012**, 134, 14430.

## Improved Performance of Artificial Metalloenzymes Based on the Biotin-Streptavidin Technology

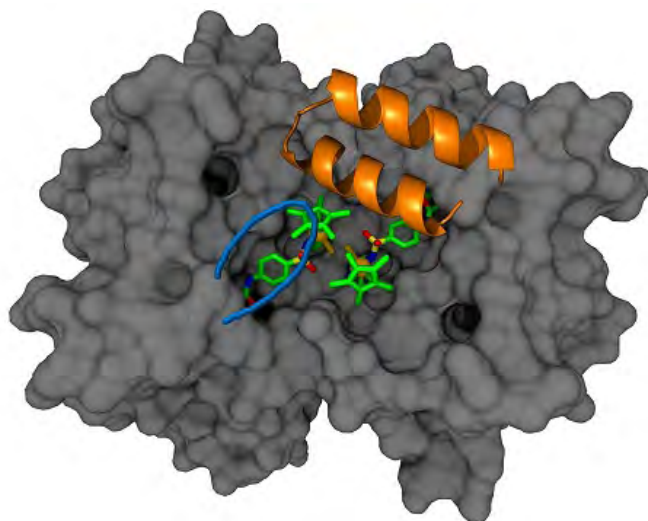
Fabian Schwizer<sup>1</sup>, Thomas R. Ward<sup>1</sup> \*

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Artificial metalloenzymes (AMEs), resulting from incorporation of an organometallic catalyst precursor into a host protein, offer new opportunities in catalysis. However, the activity of current AMEs often does not compare favourably with the protein-free metal cofactor. To address this challenge, approaches relying on the fine tuning of the second coordination sphere around the metal may be envisaged.<sup>[1]</sup>

We have recently shown that the introduction of lipophilic amino acid residues around the active site of an artificial imine reductase led to an 8-fold increase in catalytic efficiency compared to the wild-type based system and better performance than the protein-free cofactor.<sup>[2]</sup>

Engineering of the host protein by introduction of additional loops (blue) or double  $\alpha$ -helix bundles (orange) at selected positions around the active site might lead to further improvement of the performance of AMEs (Fig. 1, Streptavidin-Ir(III)complex<sup>[3]</sup>, PDB ID 3PK2). By partly closing the binding site vestibule, a very different reaction environment can be created (e.g. a mainly apolar one favouring lipophilic substrates). Additionally, the active complex might be better shielded against catalyst poisons (e.g. glutathione) and therefore catalysis in complex media may be achieved, thus potentially to run catalysis in cell free extracts or even *in vivo*.



[1] Yu, F.; Cangelosi, V. M.; Zastrow, M. L.; Tegoni, M.; Plegaria, J. S.; Tebo, A. G.; Mocny, C. S.; Ruckthong, L.; Qayyum, H.; Pecoraro, V. L. *Chem. Rev.* **2014**, *114*, 3495-3578.

[2] Schwizer, F.; Köhler, V.; Dürrenberger, M.; Knörr, L.; Ward, T. R. *ACS Catal.* **2013**, *3*, 1752-1755.

[3] Duerrenberger, M.; Heinisch, T.; Wilson, Y. M.; Rossel, T.; Nogueira, E.; Knoerr, L.; Mutschler, A.; Kersten, K.; Zimbron, M. J.; Pierron, J.; Schirmer, T.; Ward, T. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 3026-3029.

**Designer Ionic Liquids for Biomass Valorization**Sviatlana Siankevich<sup>1</sup>, Paul Dyson<sup>1</sup> \*<sup>1</sup>EPFL Lausanne

Chemical transformations of lignocellulosic substrates that afford valuable platform chemicals remain challenging. Indeed, viable catalytic systems, either biocatalysts or synthetic catalysts, are urgently needed to move away from petrochemical feedstocks that ultimately increase carbon dioxide levels in the atmosphere and are unsustainable. 5-Hydroxymethylfurfural (HMF) is a key platform chemical that may be obtained from various cellulosic (biomass) derivatives. The use of volatile and toxic organic solvents for this reaction is not ideal and consequently ionic liquids (ILs), which are non-volatile and exhibit relevant solvation properties, have been explored as alternatives. Indeed, the synthesis of HMF from fructose and glucose may be enhanced when certain ILs are employed as the reaction media. Imidazolium-based ILs display a high degree of three-dimensional structural organization relative to other ILs due to the three acidic hydrogen atoms on the imidazolium cation, aiding the directionality of hydrogen bonds and other weak forces. Consequently, introducing some specific hydrogen-bond donor/acceptor groups, and potentially other types of functionality, should enhance the ability of the IL to interact with a substrate. Such groups also influence the intermolecular interactions between ions, favoring solvent-substrate interactions and hence activation, and nascent studies indicate that functionalized ILs can enhance biomass transformations. We demonstrate that the careful design of the IL cation and the application of resulting IL-CrCl<sub>2</sub> systems, in which hydrogen-bond donor/acceptor groups on the imidazolium cation of the IL, allow HMF to be obtained from glucose in considerably higher yields compared to simple ILs. In situ NMR spectroscopy and computational modeling pinpoint the key interactions between the IL, catalyst and substrate that account for the enhanced reactivities observed. Moreover, the new system also converts more complicated substrates such as cellobiose, maltotetraose and starch into HMF in good yield.

**Room temperature Au nanoparticle deposition via control of TiO<sub>2</sub> surface chemistry**

Georges Siddiqui<sup>1</sup>, Victor Mougél<sup>1</sup>, Christophe Copéret<sup>1</sup> \*

<sup>1</sup>ETH Zurich

Though gold is usually a catalytically inert material, nanoscale Au supported on TiO<sub>2</sub> has been shown to be catalytically active for CO oxidation [1]. However the challenge with the generation of supported nanoparticles lies in obtaining contaminant free 2nm particles.

We report a unique, low temperature method for the deposition of Au nanoparticles from gold mesityl precursor onto anatase TiO<sub>2</sub>. Via dehydroxylation of TiO<sub>2</sub> at various temperatures we can control both the uniformity and particle size of Au deposited on TiO<sub>2</sub> (Figure 1). This offers a novel route for controlled, contaminant free, low temperature Au nanoparticle deposition.

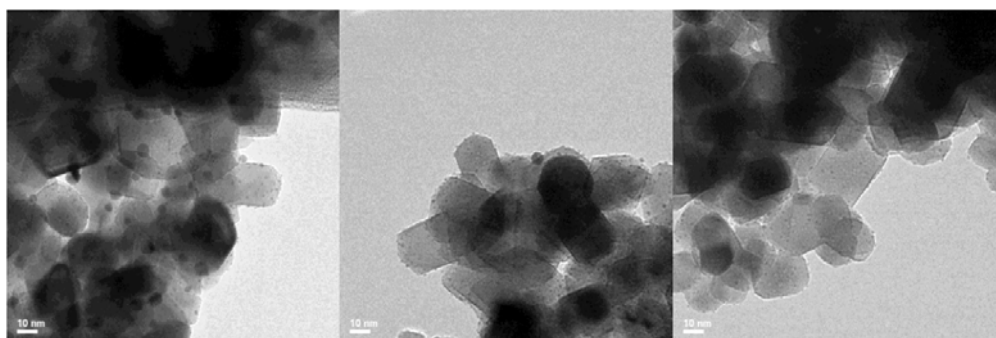


Figure 1 – TEM micrograph of Au nanoparticles deposited on TiO<sub>2</sub>. Au deposition immediately after calcination at 450°C (left) , 1.4nm average particle size, after dehydration at room temperature for 12h, 0.8nm average particle size (center), after 120°C dehydroxylation for 12h, 0.7nm average particle size (right)

[1] Haruta et al., *J. Catal.*, **1993**, 144, 175

**Asymmetric transfer hydrogenation of imines: Structural effects within Noyori-Ikariya catalysts**

Petr Šot<sup>1</sup>, Beáta Vilhanová<sup>1</sup>, Ondřej Matuška<sup>1</sup>, Marek Kuzma<sup>2</sup>, Petr Kačer<sup>1</sup> \*

<sup>1</sup>Institute of Chemical Technology, Prague, Czech Republic, <sup>2</sup>Academy of Sciences of the Czech Republic, Prague

Half-sandwich Ru-TsDPEN systems nowadays represent a well established class of catalysts employed for asymmetric transfer hydrogenation (ATH) of prochiral ketones and imines. These systems (also called Noyori-Ikariya catalysts) consist of a chiral *N*-arylsulfonylated diamine backbone (typically represented by *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine, abbr. TsDPEN), arene ligand bonded to the central atom in a  $\eta^6$  manner and counter-ion. Relatively simple chemical nature and high stability of these moieties offer great modularity; even subtle structural modifications can (and very often do) lead to strongly different behavior of the catalyst in terms of enantioselectivity, reaction rate, solubility, etc. Presented experimental and DFT computational work is dedicated especially to the modifications of two important parts: the  $\eta^6$ -arene ligand and *N*-arylsulfonyl moiety, and their influence on the asymmetric transfer hydrogenation of imines (specifically substituted 3,4-dihydroisoquinolines), which is less understood than the ATH of ketones. Our results demonstrate not only that it should be possible to tailor the properties of the catalyst specifically for each substrate, but also that there are some generic trends, for example enantiomeric excess was always higher in case of  $\eta^6$ -mesitylene and  $\eta^6$ -*p*-cymene than in case of  $\eta^6$ -benzene and  $\eta^6$ -hexamethylbenzene; on the other hand, only catalyst with  $\eta^6$ -benzene is able to hydrogenate 1-phenyl-3,4-dihydroisoquinoline.

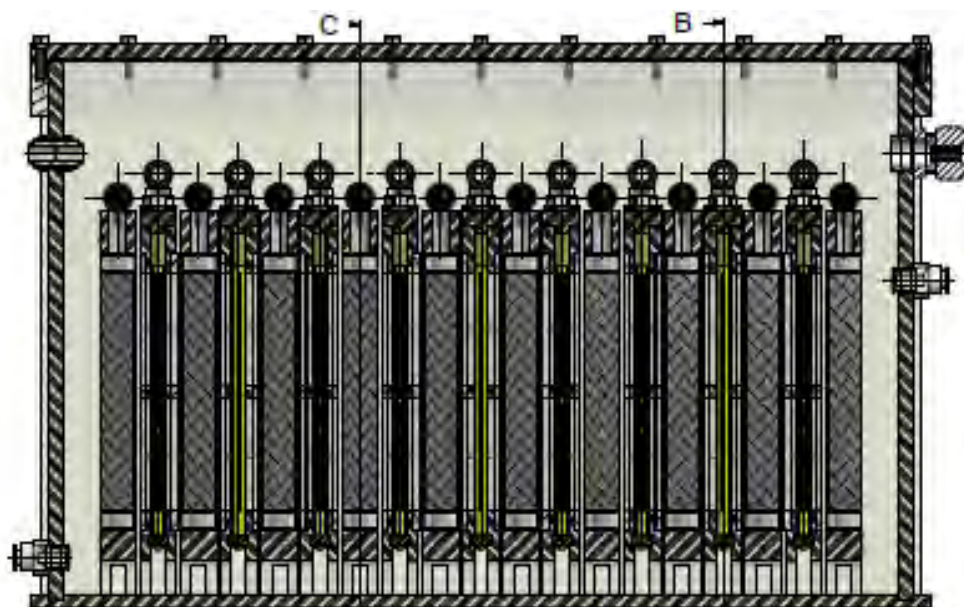
*This work has been financially supported by the Grant Agency of the Czech Republic (Grant GACR P106/12/1276) and specific university research (MSMT No 20/2014).*

**Hydrogen from activated sewage sludge with a stacked microbial electrolysis cell**

Marc Sugnaux<sup>1</sup>, Christian Pierre Cachelin<sup>1</sup>, Alain-François Grogg<sup>1</sup>, Fabian Fischer<sup>1</sup> \*

<sup>1</sup>HES-SO Valais

Activated sewage sludge contains organic substrate as well as mixed consortia of microorganisms. Microbial electrolysis cells are proposed to convert waste water constituents into hydrogen while purifying water [1]. A 20 litre stacked microbial electrolysis cell reactor was designed and constructed from reinforced polymer. This reactor consisted of 19 distinctive electrodes; the anodes were made from reticulated vitreous carbon, which were immersed in activated sewage sludge. The cathodes were based on nickel or platinum and protected with Nafion<sup>TM</sup> proton exchange membranes. These cathodes were filled with phosphate buffer and equally inserted into the stack. The metabolic degradation under an applied voltage of around ~0.7-1.5 V generated stoichiometric quantities of electrons and protons, which were fused on platinum sputtered reticulated vitreous carbon electrodes [2].



Methanogenic microbes compete with exoelectrogenic microbes such as *Geobacter* and *Shewanella* species, which are estimated to be selected by anodes from waste water. The challenge in this work is to recover as much hydrogen and methane as possible. But also to favour hydrogen production while preventing or reducing simultaneous methane formation.

[1] Minghua Zhou, Hongyu Wang, Daniel J. Hassett, Tingyue Gu, *Journal of Chemical Technology and Biotechnology*, **2013**, 88, 508-518.

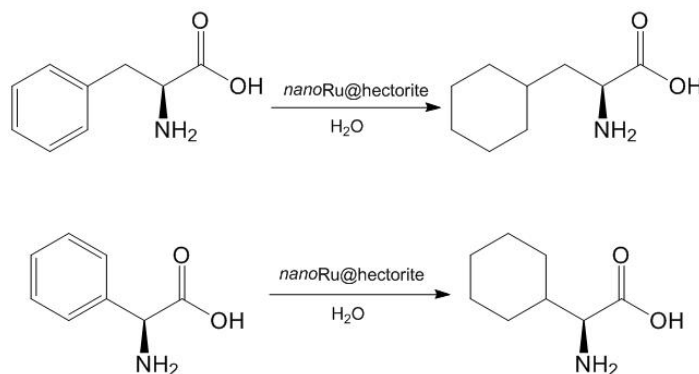
[2] Bruce E. Logan, Douglas Call, Shaoan Cheng, Hubertus V. M. Hamelers, Tom H. J. A. Sleutels, Adriaan W. Jeremiasse, René A. Rozendal, *Environmental Science and Technology*, **2008**, 23, 8630-8640.

**Selective hydrogenation of aromatic amino acids in aqueous solution catalyzed by nanoRu@hectorite**

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<sup>1</sup>University of Neuchatel

Cyclohexyl-functionalized amino acids are useful as precursors for several pharmaceuticals [1,2]. The heterogeneous catalytic hydrogenation of the corresponding phenyl substituents is an attractive method for the synthesis of these compounds.



Ruthenium nanoparticles intercalated in hectorite [3,4], selectively catalyze the hydrogenation of the phenyl substituents in L-phenylalanine and in L-phenylglycine to give L-cyclohexylalanine and L-cyclohexylglycine in aqueous solution. Both, conversion and selectivity are higher than 99%. No racemization is observed.

[1] J. R. Luly, C. -N. Hsiao, N. BaMaung, J. J. Plattner. *J. Org. Chem.* **1988**, 53, 6109-6112.

[2] R. A. Rivero, W. J. Greenlee. *Tetrahedron Lett.* **1991**, 32, 2453-2456.

[3] G. Süss-Fink, B. Mollwitz, B. Therrien, M. Dadras, G. Laurenczy, A. Meister, G. Meister. *J. Clust. Sci.* **2007**, 18, 87-95.

[4] G. Süss-Fink, F. -A. Khan, J. Boudon, V. Spassov. *J. Clust. Sci.* **2009**, 20, 341-353.



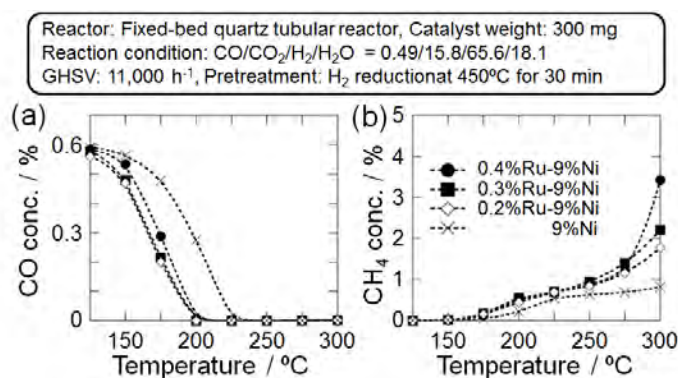
## Selective CO Methanation over Ru-Ni/TiO<sub>2</sub>: Effect of Ru and Ni Loading Amount

Shohei Tada<sup>1</sup>, Daisuke Minori<sup>1</sup>, Fumito Otsuka<sup>1</sup>, Ryuji Kikuchi<sup>1</sup> \*

<sup>1</sup>The University of Tokyo

Anode of polymer electrolyte fuel cells (PEFC) operated at low temperatures is poisoned by CO contained in reformates. It is, therefore, necessary to reduce CO concentration below 100 ppm in the reformates. CO methanation ( $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ ) has been regarded as a possible method to abate CO in the reforming gases. Simultaneous CO<sub>2</sub> methanation ( $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ ) is, however, an undesirable reaction in the CO removal because of highly exothermic nature and huge consumption of H<sub>2</sub>. Consequently, a suitable catalyst must be developed to promote CO methanation and inhibit coincident CO<sub>2</sub> methanation. In our previous study, Ru-Ni/TiO<sub>2</sub> exhibited high CO methanation activity and low CO<sub>2</sub> methanation activity [1], and kept them for more than 5,500 h at a high space velocity of 10,000 h<sup>-1</sup> [2]. This was probably because in Ru-Ni/TiO<sub>2</sub> most of the Ru resides on top of the Ni species and consequently the active interface between Ru and TiO<sub>2</sub> for CO<sub>2</sub> methanation [3] is decreased [1]. In this study, xwt%Ru-ywt%Ni/TiO<sub>2</sub> catalysts (x = 0, 0.2, 0.3, 0.4, y = 0, 5, 9) were prepared, and the effect of the metal loading on activity and selectivity of CO methanation was investigated.

The figure shows (a) CO and (b) CH<sub>4</sub> concentration against reaction temperature over the prepared catalysts. The CO concentration dropped rapidly against temperature on Ru-Ni/TiO<sub>2</sub> with a decrease in the Ru loadings. The CH<sub>4</sub> concentration, reflected in the activity of RWGS reaction, increased slowly with a decrease in the Ru loadings. Consequently, the 0.2wt%Ru-9wt%Ni/TiO<sub>2</sub> was the most suitable for selective CO methanation. The catalyst produced little CO from CO<sub>2</sub> due to the activity of RWGS reaction, resulting in rapid abatement of CO at low temperatures and low production of CH<sub>4</sub> at high temperatures compared to 0.3wt%Ru-9wt%Ni/TiO<sub>2</sub> and 0.4wt%Ru-9wt%Ni/TiO<sub>2</sub> [4].



[1] Shohei Tada, Ryuji Kikuchi, Atsushi Takagaki, Takashi Sugawara, Shigeo Ted Oyama, Kohei Urasaki, Shigeo Satokawa, *Applied Catalysis B: Environmental*, **2013**, 140-141, 258-264.

[2] Shohei Tada, Ryuji Kikuchi, Katsuya Wada, Kazuo Osada, Kazuya Akiyama, Shigeo Satokawa, Yoshimi Kawashima, *Journal of Power Sources*, **2014**, 264, 59-66.

[3] Paraskevi Panagiotopoulou, Dimitris I. Kondarides, Xenophon E. Verykios, *The Journal of Physical Chemistry C*, **2011**, 115, 1220-1230.

[4] Shohei Tada, Daisuke Minori, Fumito Otsuka, Ryuji Kikuchi, Kazuo Osada, Kazuya Akiyama, Shigeo Satokawa, *Fuel*, **2014**, 129, 219-224.

**Tuning electrocatalytic activity of Pt for oxygen reduction by structure modification**

Sandra Temmel<sup>1</sup>, Daniele Pergolesi<sup>2</sup>, Emiliana Fabbri<sup>2</sup>, Rüdiger Kötz<sup>2</sup>, Thomas Lippert<sup>2</sup>, Thomas Schmidt<sup>2</sup> \*

<sup>1</sup>Paul Scherrer Institute, Villigen and ETH Zurich, <sup>2</sup>Paul Scherrer Institute, Villigen

Polymer electrolyte fuel cells (PEFCs) represent a promising technology for converting chemical energy into electricity with the only waste product water. However, the main obstacle towards their successful commercialization is their high cost, originating from the use of the expensive precious metal catalyst. The electrochemical reactions proceeding in this PEFCs anodes and cathodes are both catalyzed best by Pt-based material. Nevertheless, the oxygen reduction reaction (ORR) occurring on the cathode is intrinsically very slow, leading to high overpotentials and performance loss. High Pt loadings are, therefore, necessary to compensate the slow kinetics. As a result, several approaches are under investigation for improving the activity of the electrocatalyst and to reduce the necessary amount of Pt. One possibility which is explored is tailoring the crystallographic orientation and/or the interatomic distance of the Pt atoms (reference). These features can be controlled by fabricating thin, epitaxial Pt films using pulsed laser deposition (PLD).

First steps towards producing such model catalysts with different crystallographic orientation and/or interatomic distance of Pt atoms are represented here. Epitaxial thin Pt films were grown by PLD on (001) and (111)-oriented SrTiO<sub>3</sub> single crystalline substrates with varying deposition parameters. X-ray diffraction measurements were carried out to determine the crystallographic orientation. The morphology was examined by scanning electron and atomic force microscopy, respectively. To probe the catalytically active surface area and to unravel possible correlations between the thin film orientation and the surface reactivity, cyclic voltammograms were recorded at room temperature in Ar-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>. ORR was measured in a home-made flow cell set up to examine the reaction kinetics under defined mass-transport conditions.

## DNP NMR Spectral Signatures of the Active Sites in Sn-Beta Zeolite and Reaction with Probe Molecules

Maxence Valla<sup>1</sup>, Patrick Wolf<sup>2</sup>, Aaron Rossini<sup>3</sup>, Aleix Comas-Vives<sup>1</sup>, Lyndon Emsley<sup>3</sup>, Ive Hermans<sup>2</sup>, Christophe Copéret<sup>1</sup> \*

<sup>1</sup>ETH Zurich, <sup>2</sup>University of Wisconsin-Madison, <sup>3</sup>Centre de RMN à très hauts champs

Sn-beta zeolites are remarkable catalysts, [1] which exhibits outstanding activity in numerous reactions including the Lewis acid catalyzed isomerization and epimerization of sugars in water allowing the upgrading of cellulose-based renewable feedstock [2]. Despite its very promising performances and its easy synthesis [3], the structure of the active sites of Sn-beta remains unknown despite intense debate in the literature. [1-4]

Various experimental investigations discuss the presence of several sites, *i.e.* closed Sn<sup>IV</sup> with four OSi linkage and opened Sn<sup>IV</sup> with three OSi linkage with the zeolite framework. While <sup>119</sup>Sn solid-state NMR spectroscopy is an ideal method to probe the Sn-IV environment, only low signal to noise ratio can be obtained even for <sup>119</sup>Sn labeled samples due to the low sensitivity of NMR. Nevertheless, signal between -685 ppm and 700 ppm could be observe assigned to be octahedral Sn-IV sites whereas signal dehydrated samples were characterized by a signal between -425 and -445 ppm (tetrahedral Sn-IV sites) [4]. However precise structure of the active sites remains unknown.

To overcome the low sensitivity of NMR, we used Dynamic Nuclear Resonance Surface Enhanced NMR spectroscopy (DNP-SENS) to obtain the NMR signatures of the active sites. In particular <sup>1</sup>H-<sup>119</sup>Sn Cross Polarization Magic Angle Turning (CPMAT) was critical to measure the chemical shift anisotropy parameters of different sites. Together with calculations and kinetic studies, it was possible to propose structures for the active sites and to attributed the NMR signature to specific octahedral Sn structures with opened and closed sites, surrounded by water in the second coordination sphere [5].

**Acknowledgement.** We would like to thank F. Nunez-Zarur, B. Malaman and A. Lesage for their contribution to the presented work.

[1] Y. Román-Leshkov, M. Davis, *ACS Catalysis* **2011**, 1, 1566.

[2] A. Corma, H. García, *Chem. Rev.* **2003**, 103, 4307.

[3] C. Hammond, S. Conrad, I. Hermans, *Angew. Chem. Int. Ed.* **2012**, 51, 11736.

[4] R. Bermejo-Deval, R. Gounder, M. E. Davis, *ACS Catalysis* **2012**, 2, 2705.

[5] P. Wolf, M. Valla, A. Rossini, A. Comas-Vives, F. Núñez-Zarur, B. Malaman, A. Lesage, L. Emsley, C. Copéret, I. Hermans, **2014**, *Manuscript submitted*.

## Mesoporous mixed oxides of cerium and zirconium modified with Au and Cu - synthesis, characterization and performance in glycerol oxidation

Jeroen A. van Bokhoven<sup>1</sup>\*, Piotr Kaminski<sup>2</sup>, Maria Ziolek<sup>3</sup>

<sup>1</sup>ETH Zurich and Paul Scherrer Institute, Villigen, <sup>2</sup>Adam Mickiewicz University in Poznan and ETH Zurich, <sup>3</sup>Adam Mickiewicz University in Pozna?

We introduce the synthesis of mesoporous ceria, zirconia and mixed oxides of cerium and zirconium modified with gold and/or copper, their characterization and application in oxidation of glycerol. Catalytic activity of catalysts was studied in oxidation of glycerol in aqua solution of NaOH and in the atmosphere of pure oxygen (6 atm) using stainless steel autoclaves and analyzed by the quadrupole mass spectrometer and the liquid chromatography. Gold was introduced to the materials using tetrachloroauric acid ( $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$ ) as a source of noble metal (1.5 wt % Au was assumed) and urea as compound to control the size of gold particles. Copper was added on the surface of the oxides by *incipient wetness impregnation* (2 wt % Cu) according to [1]. The fresh samples modified with gold contained both metallic  $\text{Au}^0$  and cationic  $\text{Au}^{\delta+}$ . In the monometallic copper containing metal oxides copper species were present as isolated  $\text{Cu}^{2+}$  with octahedral coordination and small oxides clusters (CuO-like species). The presence of gold on the surface of oxides with cerium caused much easier reduction of CuO-like species and higher mobility of oxygen. The results of STEM-EDXS analysis which were obtained for the bimetallic Cu-Au catalysts evidenced that gold is in the form of metallic nanoparticles and is located in the neighbourhood of copper species (Fig. 1.). The size distribution of gold particles in these materials is not homogenous.

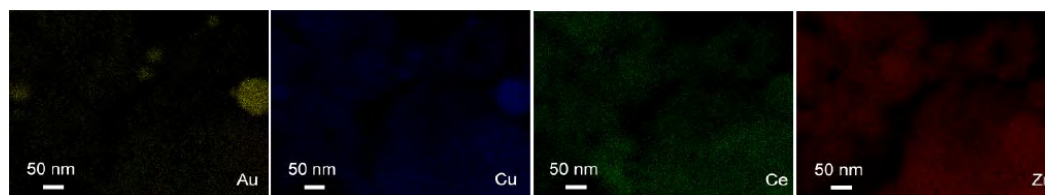


Fig. 1. STEM images performed for the fresh CuAu/CeZrO<sub>x</sub> (as assumed CeO<sub>2</sub>:ZrO<sub>2</sub> = 1:1).

The results show that in the bimetallic catalysts there is direct interaction between cationic copper species and metallic gold particles affecting the catalytic performance. Gold nanoparticles are thus promoted by the oxidative properties of copper, making the bimetallic Cu-Au oxides of cerium and zirconium a promising material for oxidation processes in the liquid phase.

**Acknowledgements:** National Science Centre in Poland (Project No. 2011/01/B/ST5/00847) is acknowledged for the financial support and P. K. is thankful for the financial support of the SCIE X NMS-CH Programme.

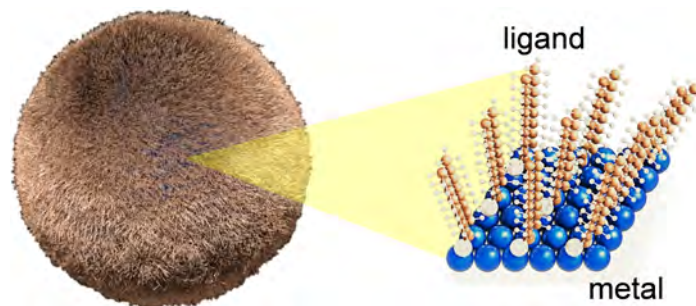
[1] P. Kaminski, M. Ziolek, J. Catal., **2014**, 312, 2147-2159.

## Chemoselective hydrogenation of functionalized nitroarenes over ligand-modified platinum nanoparticles

Gianvito Vilé<sup>1</sup>, Neyvis Almora-Barrios<sup>2</sup>, Gastón Larrazábal<sup>1</sup>, Núria López<sup>2</sup>, Javier Pérez-Ramírez<sup>1</sup> \*

<sup>1</sup>ETH Zurich, <sup>2</sup>ICIQ

The hydrogenation of aromatic nitro-compounds over V- and Pb-poisoned platinum catalysts is the method of choice for the production of functionalized anilines, which are valuable intermediates in the manufacture of agrochemicals, pharmaceuticals, dyes, and pigments.<sup>1</sup> The recent emergence of ligand-modified Pt nanoparticles (Fig. 1) matching the chemoselectivity of the archetypal catalysts, without the need of poisons in the catalyst formulation,<sup>2</sup> holds promise to revolutionize this type of reaction. In this work, we compare the performance of bare, vanadium- or lead-poisoned, and ligand-modified platinum catalysts to that of silver- and gold-based catalysts in the hydrogenation of diverse nitroarenes under flow chemistry operation. The observed chemoselectivity patterns are elucidated by means of characterization methods, molecular simulations, and microkinetic analyses. Accessibility constraints derived from the presence of the ligands are also highlighted. Our findings provide directions for the design of improved supported Pt catalysts for nitroarene hydrogenation.



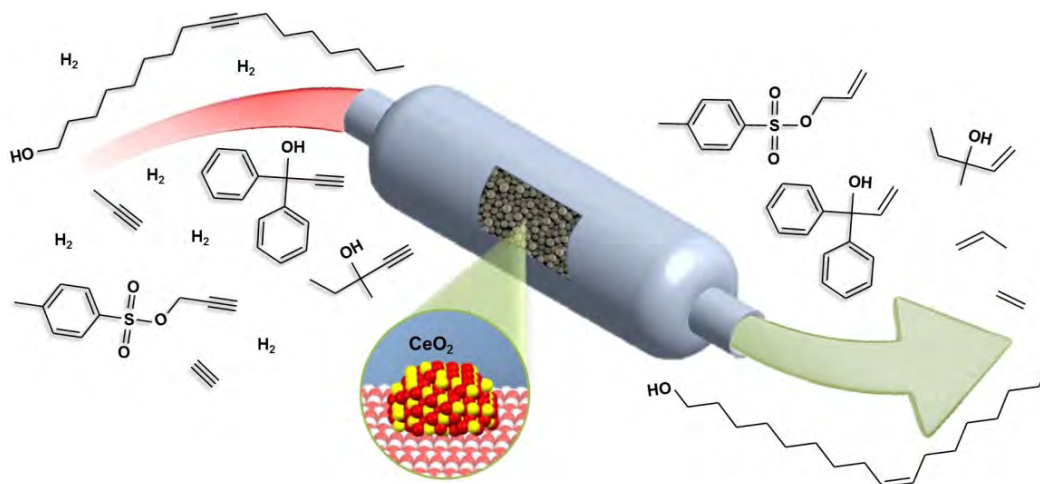
**Figure 1.** Schematic representation of the ligand-modified platinum nanoparticles.

1. H.-U. Blaser, H. Steiner, M. Studer, *ChemCatChem* **2009**, 1, 210.

2. E. Boymans, S. Boland, P.T. Witte, C. Müller, D. Vogt, *ChemCatChem* **2013**, 5, 431.

**Selective hydrogenation of alkynes over CeO<sub>2</sub>-based catalysts**Gianvito Vilé<sup>1</sup>, Javier Pérez-Ramírez<sup>1</sup> \*<sup>1</sup>ETH Zurich

Ceria is a critical component in a variety of oxidation reactions, where it is used as a support, stabilizer, promoter, or active phase. The recent discovery that pure CeO<sub>2</sub> efficiently catalyzes the semi-hydrogenation of alkynes has broadened its scope in catalysis. A high specific surface area and the absence of oxygen vacancies are known to be important characteristics for attaining high olefin yields,<sup>1</sup> and DFT calculations have revealed a possible reaction mechanism for acetylene hydrogenation.<sup>2</sup> Continuous-flow liquid-phase hydrogenations of bulkier acetylenic compounds have further highlighted the outstanding chemo- and stereoselectivity of supported CeO<sub>2</sub> (Fig. 1), which exceeds the performance of the conventional Lindlar catalyst.<sup>3</sup> In this contribution, we revisit recent developments in the field of ceria-catalyzed alkyne hydrogenation, providing an outlook into future directions for research. Particularly, we explore strategies, e.g., the preparation of model particles with distinct morphology and the doping of CeO<sub>2</sub>, to enhance the hydrogenation activity of CeO<sub>2</sub>, enabling the understanding of structure-performance relationships and low-temperature and low-pressure operation.



**Figure 1.** Schematic representation of the hydrogenation of different acetylenic compounds over CeO<sub>2</sub>-based catalysts.

1. G. Vilé, B. Bridier, J. Wichert, J. Pérez-Ramírez, *Angew. Chem., Int. Ed.* **2012**, 51, 8620.
2. J. Carrasco, G. Vilé, D. Fernández-Torre, R. Pérez, J. Pérez-Ramírez, M.V. Ganduglia-Pirovano, *J. Phys. Chem. C* **2014**, 118, 5352.
3. G. Vilé, S. Wrabetz, L. Floryan, M.E. Schuster, F. Girgsdies, D. Teschner, J. Pérez-Ramírez, *ChemCatChem* **2014**, doi:10.1002/cctc.201402124.



## Highly periodic catalyst nanostructures for the production of sustainable energy

Roche Marcel Walliser<sup>1</sup>, Artur Braun<sup>2</sup>, Catherine E. Housecroft<sup>1</sup>, Edwin C. Constable<sup>1</sup> \*

<sup>1</sup>University of Basel, <sup>2</sup>EMPA Dübendorf

Cheap, green and sustainable energy production is one of the greatest wishes of our time. Hydrogen fuel induced by solar water splitting is a vision of the future which can allay our needs. One part of the research in our group is focused on the cheap and sustainable production of solar energy. My research is focused on the fabrication of low cost, environmentally friendly nano-scale surfaces and systems which show catalytic properties. Therefore we used several techniques and systems which could possibly be used to produce very cheap, easily reproducible and highly catalytically active surfaces. With the combination of the WET-stamping [1] techniques and Liesegang phenomena [2] we are able to form highly periodic nano-structures (Fig. 1). Together with our research collaboration we used these nano-lithographic technique for the production of nanostructures made out of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) (Fig. 2) or ruthenium(II) coordination compounds (Fig. 3). Hematite nanoparticles (rust) can be used to produce hydrogen fuel by artificial solar water-splitting [3] and ruthenium(II) coordination compounds can be used in catalysis (e.g. for artificial water-splitting, aqueous hydration) [4,5].

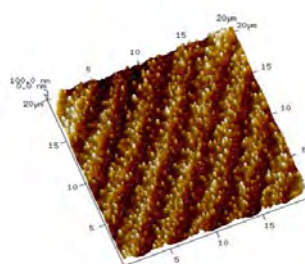


Figure 1 – AFM of patterned structure

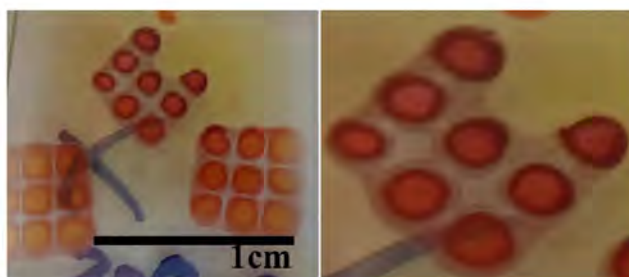


Figure 2 - Hematite-nanoparticle patterned structure

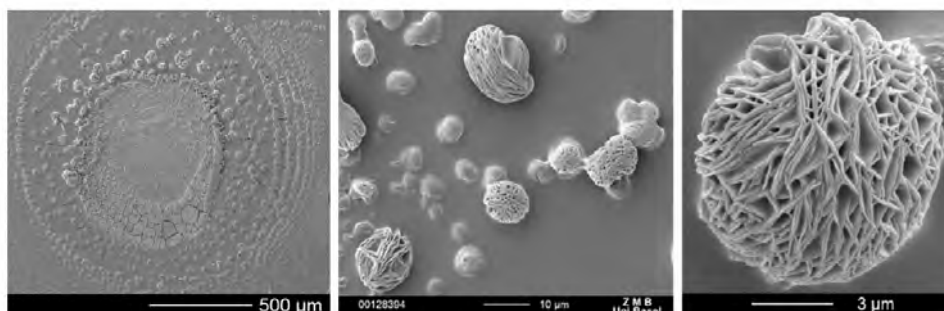


Figure 3 - Ruthenium (II) coordination compound micro-bands with nanoparticles

[1] C. J. Campbell, E. Baker, A. Bitner, S. K. Smoukov, B. Grzybowski, *J. Appl. Phys.* **2005**, 97, 126102.

[2] I. Lagzi, *Langmuir* **2012**, 28, 3350.

[3] D. K. Bora, A. Braun, E. C. Constable, *Energy Environ. Sci.* **2013**, 6, 407.

[4] L. Duan, Y. Xu, P. Zhang, M. Wang, L. Sun, *Inorg. Chem.* **2010**, 49, 209.

[5] C. K. Prier, D. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, 113, 5322.

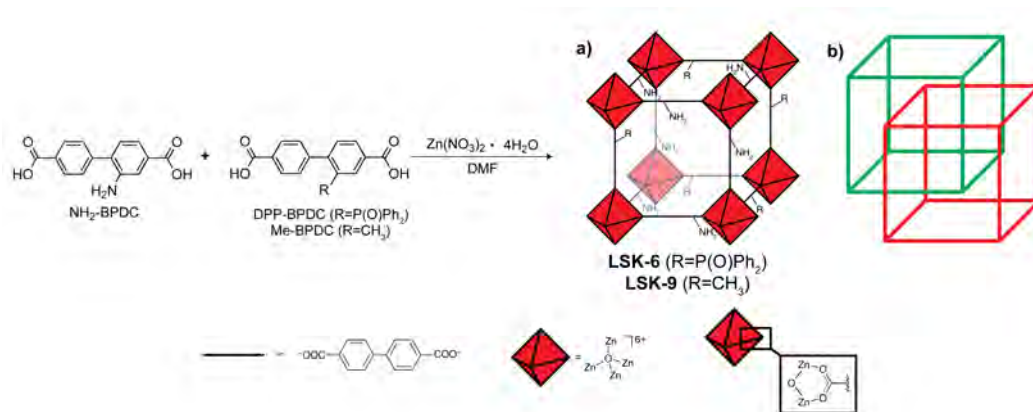


## Tuning Regioisomer Reactivity in Catalysis using Bifunctional Metal-Organic Frameworks with Mixed Linkers

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Metal-organic frameworks (MOFs) are potential materials for many applications, including heterogeneous catalysis.[1] Here, we describe two bifunctional MOFs with IRMOF-9 topology, named LSK-6 and LSK-9 and containing amino, diphenylphosphoryl (DPP) and methyl groups. These three functional groups act cooperatively to induce a unique catalytic response. The amino group acts as an active site for Knövenagel condensation reactions, while the phosphine oxide and methyl groups moderate the spatial characteristics inside the MOF pores.



Reactions between *ortho*, *meta* respectively *para* nitrobenzaldehyde and malononitrile over the DPP containing MOF showed decreased reactivity of the *ortho* isomer compared to the methyl-group containing one.[2] Steric impediments have less of effect upon reactions involving the less hindered *para* and *meta* benzaldehydes. This finding further encourages research toward tailor-made MOFs, to fine-tune reaction reactivity by modifying the steric properties of porous heterogeneous catalysts.

[1] M. Ranocchiari, J. A. van Bokhoven, *Phys. Chem. Chem. Phys.* **2011**, 13, 6388.

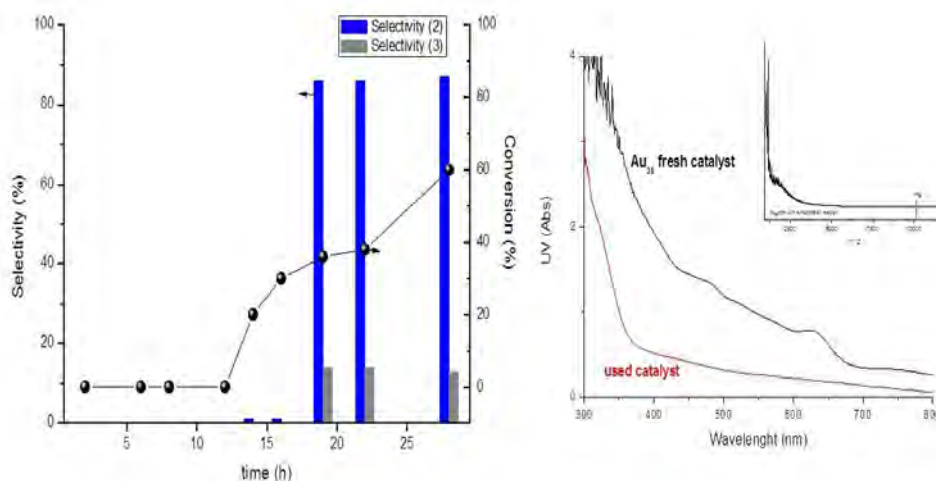
[2] X. Xu, J. A. van Bokhoven, M. Ranocchiari, *ChemCatChem*, **2014**, accepted.

## Gold thiolated clusters $\text{Au}_{38}(\text{SR})_{24}$ in oxidation reactions

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In the latest years, application of protected thiolated gold nanoclusters in catalysis has been emerged, leading to well-defined and homogeneous systems<sup>1</sup>. It represents an attractive system for *in situ* reaction mechanism studies. In addition, catalytic activity with  $\text{Au}_x(\text{SR})_n$  clusters in oxidation and hydrogenation reaction is enhanced with respect to Au catalysts. It opened a new line of research in the gold catalysis field. Most of the catalytic studies have been focused on  $\text{Au}_{25}(\text{SR})_{18}$  due to the magic number stability configuration and the possibility of different electronic states<sup>2</sup>. Several catalytic studies performed using unsupported clusters indicated high catalytic activity despite the coordination of thiol ligands in the gold surface, one of the most common poison in metal catalysis. The understanding of the catalytic activity of the clusters represents a key point for extended application. In order to study the stability of these clusters in reactive media, sulfoxidation reaction with  $\text{Au}_x(\text{SR})_n$  has been studied and characterized in situ by UV-vis, MALDI and XANESS. These measurements reveal the direct relation of the catalytic activity with the decomposition of the gold cluster into small units.



[1] G.Li, et al., *Accounts of Chemical Research* **2013**, 46, 1749.

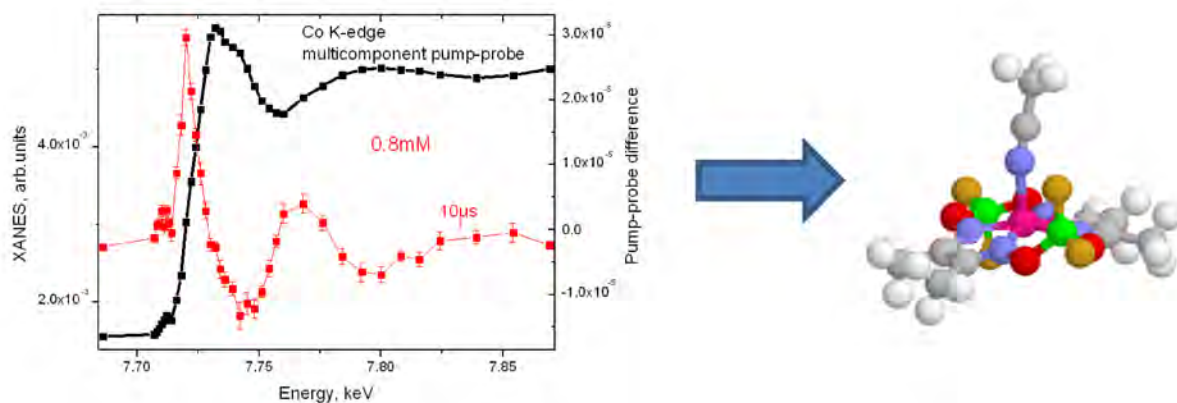
[2] C.S.S.R.Kumar, et al., *Chemistry- A European Journal* **2013**, 19, 10201.

## The structure of intermediates of cobaloxime H<sub>2</sub> evolving photo-catalyst refined by X-ray absorption spectroscopy with sub-microsecond time resolution

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Rational design of molecular catalysts for hydrogen evolution from water using sunlight is a challenging task of great scientific and practical importance. The research in this field strongly benefits from the detailed understanding of the local atomic and electronic structure of reaction intermediates. In order to get this information with high temporal ( $\sim 0.5$  microsecond) and spatial ( $\sim 0.03$  Angstrom) resolution for metal complexes in solution we have developed a new setup for laser-initiated time-resolved X-ray absorption (XAS) measurements at SuperXAS beamline of SLS synchrotron. It has been applied to study a few multicomponent photocatalytic systems with cobaloxime catalysts in combination with Ru-based or organic chromophores. It has been found that irrespective of the oxidation state of Co in cobloxime before light illumination, the dominant oxidation state of Co at catalytic conditions is 2+. We have observed the formation of Co<sup>+</sup> and Co<sup>3+</sup>H intermediates and their structure has been determined on the basis of analysis of the series of hundreds of Co K-edge XAS spectra corresponding to different delay times after the laser excitation of the chromophore. Calculated X-ray transient signal for a model of Co(I) state with a 0.14 Å displacement of Co out of the ligand plane and with the closest solvent molecule at a distance of 2.06 Å gives good agreement with the experimental data.

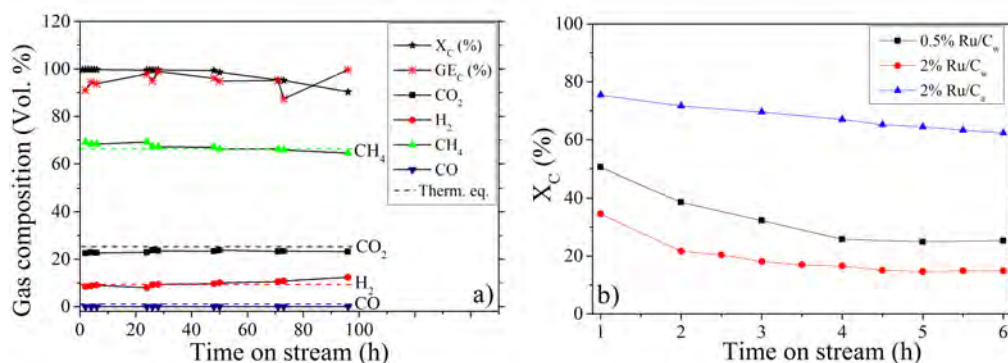


## Carbon-supported Ru as a Catalyst for Supercritical Water Gasification of Isopropanol for Methane Production

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Catalytic supercritical water gasification (CSCWG) is a promising technology to convert efficiently wet biomass (e.g. microalgae, biomass residues) to biomethane. Although the Ru/C catalysts were reported[1]to have good catalytic performance,there is still a necessity to assess some relevant parameters related to the catalyst design for the catalyst optimization. Here, we studied the Ru dispersion effect and the effect of the solvent (water vs acetone) used during the catalyst preparation by carrying out CSCWG with isopropanol as an organic model compound. The Ru/C catalysts were prepared by wet impregnated with  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  precursor in a water ( $\text{Ru}/\text{C}_w$ ) or in an acetone ( $\text{Ru}/\text{C}_a$ ) solution and characterized by HAADF-STEM and XPS. The catalytic performance was assessed with a fixed-bed plug flow reactor (450 °C, 30 MPa) with 10 wt. % isopropanol in water. In **Fig. 1. (a)** the 2%  $\text{Ru}/\text{C}_a$  was able to gasify efficiently isopropanol during 96 hours at a  $\text{WHSV}_{\text{gRu}} = 1228 \text{ g}_{\text{Org}}/\text{g}_{\text{Ru}} \cdot \text{h}$  with a gas composition close to the thermodynamic chemical equilibrium. The similarity between the observed activity ( $X_c$ ) and the carbon gasification efficiency ( $\text{GE}_c$ ) proves that the carbon contained in the feed is fully converted to the gases. In **Fig. 1. (b)**, at  $\text{WHSV}_{\text{gRu}} = 5202 \text{ g}_{\text{Org}}/\text{g}_{\text{Ru}} \cdot \text{h}$ , a relevant effect of the Ru dispersion (D) was found where the 0.5%  $\text{Ru}/\text{C}_w$  (D = 37%) exhibited a higher activity than the 2%  $\text{Ru}/\text{C}_w$  (D = 18%). The use of acetone improves the Ru dispersion (D = 35%) and reduces significantly the amount of residual chloride on the catalyst resulting in a higher activity for the 2%  $\text{Ru}/\text{C}_a$ .



[1] M.H. Waldner, F. Krumeich, F. Vogel, *Journal of Supercritical Fluids*, **2007**, 43, 91-105.