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Poster Abstracts

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**Novel approaches for the biosynthesis of tailor-made polyhydroxyalkanoates**C. Utsunomia<sup>1</sup>, N. Hanik<sup>1</sup>, M. Zinn<sup>1\*</sup><sup>1</sup>HES-SO Valais, Institute of Life Technologies

Polyhydroxyalkanoates (PHA) are representative biopolyesters that are microbially synthesized and generally are biodegradable and biocompatible. Typically, transesterification of hydroxyalkanoic acids as monomers is catalyzed by a PHA synthase yielding high-molecular weight polyesters that are intracellularly accumulated [1]. In nature, PHA are commonly found in the forms of poly(3-hydroxybutyrate) (P3HB) and of random copolymers containing 3-hydroxyvalerate (3HV), 3-hydroxyhexanoate (3HHx) and other 3-hydroxyalkanoates. To improve the competitiveness of PHA facing conventional petroleum-based polymers, achieving tailor-made structures (e.g., homo- and block-copolymers) is a promising approach for the development of new and favorable material properties. Block-copolymers are polymer chains that contain blocks of different monomers covalently linked together. Such structures potentially undergo microphase separation to form periodic nanostructures which can lead to unique physical properties [2]. Here, our goal is to develop cultivation systems for the microbial production of well-defined PHAs. First, bioprocesses will be established for the biosynthesis of PHA homo- and random copolymers and afterwards the fermentation design will be adapted for accomplishing the all *in vivo* production of PHA block-copolymers. Besides the environmental aspect, one of the major advantages of the biosynthetic system is the generation of polyesters with molecular weight ranging from several ten thousands to several million Daltons, which is not easily obtained via chemical synthesis. As a starting point of this research, we have been investigating the gram-negative and native PHA-producer *Comamonas acidovorans* DSM 4746 for the production of poly(4-hydroxybutyrate) (P4HB) using the low-cost substrate 1,4-butanediol (1,4-BDO). Either P4HB and poly(4-hydroxybutyrate-co-3-hydroxybutyrate) could be successfully produced although at a low yield. We have identified the uptake of 1,4-BDO into the cells as one of the limiting steps for the efficient polymer production. Further improvement of the biosynthetic system will be carried out together with the establishment of an optimized bioprocess. Such workflow will be adopted for the production of tailor-made PHA serving as building blocks for further block-copolymer syntheses.

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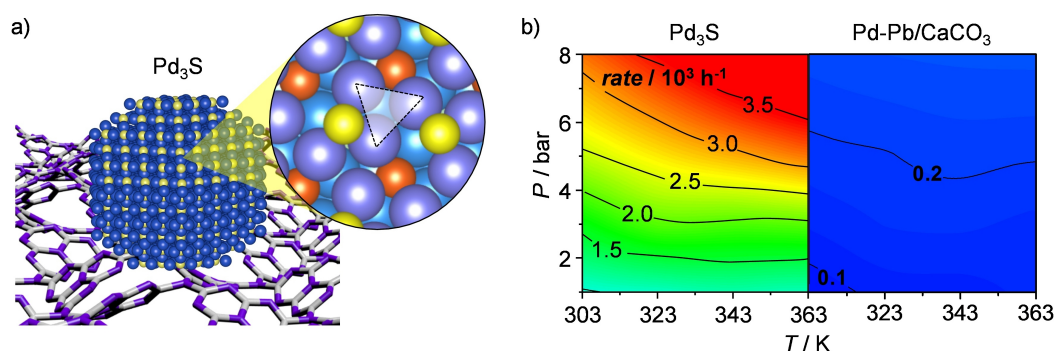
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## Selective ensembles in supported palladium sulfide nanoparticles for alkyne semi-hydrogenation

D. Albani<sup>1</sup>, M. Shahrokhi<sup>2</sup>, Z. Chen<sup>1</sup>, S. Mitchell<sup>1</sup>, N. López<sup>2</sup>, J. Pérez-Ramírez<sup>1\*</sup>

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The ultimate mission of researchers working in heterogeneous catalysis is the identification of active ensembles with a high density to enable efficient turnover while avoiding undesired intermolecular interactions, and exhibiting long-term stability to ensure a well-defined performance. The fulfillment of all these requirements in one catalytic material has yet to be accomplished, even for well-established reactions like the partial hydrogenation of alkynes. For decades ensemble control has been intensively pursued to uncover sustainable alternatives to the Lindlar catalyst (Pd-Pb/CaCO<sub>3</sub>) applied for the partial hydrogenation of alkynes in industrial organic synthesis.<sup>1</sup> Despite knowing the geometric and electronic parameters required to tune the ensemble characteristics, a literature survey illustrates the difficulty of transferring this knowledge into an efficient and robust catalyst. This study reports a simple treatment of palladium nanoparticles supported on graphitic carbon nitride with aqueous sodium sulfide, which directs the formation of a nanostructured Pd<sub>3</sub>S phase with controlled crystallographic orientation, exhibiting unparalleled performance in the three-phase semi-hydrogenation of alkynes (Figure 1).<sup>2</sup> The exceptional behavior is linked to the multifunctional role of sulfur. Apart from defining a structure integrating spatially-isolated palladium trimers, the active ensembles, the modifier imparts a bifunctional mechanism and weak binding of the organic intermediates. Similar metal trimers are also identified in Pd<sub>4</sub>S, evidencing the pervasiveness of these selective ensembles in palladium sulfide phases.



**Figure 1** a) Structure of the supported Pd<sub>3</sub>S nanoparticle. The inset depicts the most stable surface termination and the corresponding ensemble is outlined with a dashed triangle. b) Contour plots mapping the rate of alkene formation as a function of temperature and pressure.

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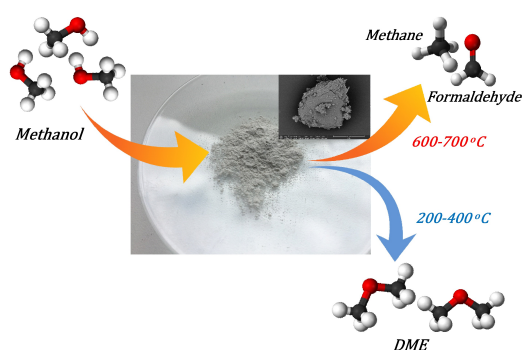
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## K10 montmorillonite clay as an environmentally friendly catalyst for methanol dehydration reaction

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As a clean non-petroleum based sustainable fuel, dimethyl ether (DME) has gained more attention recently for potential diesel replacement. Here in this study, we introduce an eco-friendly, inexpensive, and naturally-made material as an active catalyst for DME synthesis through methanol dehydration reaction. Through our experiments, K10 montmorillonite clay (acid-treated montmorillonite clay) showed very high DME selectivity (nearly 100%) and activity for methanol conversion (80%) at 300°C. However, at higher operating temperatures, the selectivity shifted towards formation of formaldehyde, methane, and carbon monoxide. Based on Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) using pyridine adsorption, we observed that catalyst activity for DME formation was correlated with the density of the Brønsted acid sites on the catalyst surface. Calcination of K10 montmorillonite clay at 300°C enhanced the catalyst performance for DME production due to desorption of chemisorbed water and modification of the catalyst surface acidity. However, higher calcination temperatures negatively affected activity and the catalyst structure as evidenced by X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), and solid state Nuclear Magnetic Resonance (MAS NMR).



## Etched Nickel Foam as Highly Efficient Catalyst for Overall Water Splitting

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Water splitting into hydrogen and oxygen is one of the most important challenges in the field of sustainable energy research and it is becoming an essential strategy for renewable and green energy generation.<sup>[1]</sup> Electrocatalytic hydrogen production can potentially solve the rising energy demand of global society. Currently, the most active materials for electrocatalytic water splitting are iridium and platinum-based catalysts for oxygen evolution reaction (OER) and hydrogen evolution reactions (HER), respectively.<sup>[2]</sup> Conspicuously, the rarity of these precious noble metals make a big obstacle to scale-up them for economical purposes. In recent decades, several efforts have been put forward to design efficient and stable water splitting catalysts based on transition-metal elements, which are earth-abundant and offer a prima facie structure alternative to precious metals-catalysts. Nickel foam, a low cost and commercially available material, has been widely applied as an electrode for overall water splitting, because of its good electronic conductivity, large surface area, porous structure, and high activity.<sup>[3]</sup> Therefore, its optimization is a sustainable way to design efficient catalysts for electrochemical hydrogen generation. In this work, the etched nickel foam catalyst was synthesized and characterized by powder XRD, XPS, FT-IR, Raman, SEM and HRTEM. In addition, the activity of this catalyst during OER and HER was studied with cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). Results showed that etching process has a significant effect on the electrochemical OER and HER activity of nickel foam.

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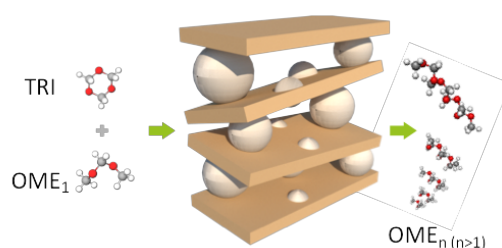
## Investigation of the catalytic performance of tin-montmorillonite clay for the synthesis of polyoxymethylene dimethyl ethers (OME)

C. J. Baranowski<sup>1</sup>, A. Bahmanpour<sup>1</sup>, O. Kröcher<sup>1,2\*</sup>

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Recently, clay has gained attention as an eco-friendly catalyst support due to its natural layered structure and high capacity for ion exchange. Introducing tin in the structure of montmorillonite clay (MMT) can form a hierarchical material (Sn-MMT) that can catalyze various acidic reactions.<sup>[1]</sup> Despite studies on its structure, little information has been provided on the source of its acidity. As an acid catalyzed reaction, synthesis of polyoxymethylene dimethyl ethers (OME) has been investigated in this study. OME are appealing, functionalized fuels or fuel additives which can be used in diesel engines to help soot-free fuel combustion.<sup>[2]</sup> Sources of methyl- and oxymethylene-group as well as an acid catalyst are required for their synthesis. Their physical and chemical properties depend strongly on their chain length; OME possessing 3 to 5 CH<sub>2</sub>O units (OME<sub>3-5</sub>) are the most desirable products.

We investigated the synthesis of OME through trioxane reaction with dimethoxymethane (OME<sub>1</sub>) catalyzed by MMT. Sn-MMT was compared with acid-treated MMT (AT-MMT) as another potential catalyst for this reaction. Various characterization techniques such as solid-state NMR and electron microscopy were used to comprehend and confirm the structure of these catalysts. Their acidity was characterized through FTIR pyridine adsorption and ammonia-TPD. Despite showing no preferential selectivity towards OME<sub>3-5</sub> synthesis, Sn-MMT demonstrated high activity for OME synthesis, comparable to acidic resins which are widely used in industry. Modification of the MMT structure through insertion of tin and, consequently, formation of SnO<sub>2</sub> nanocrystals between the clay layers boosted the catalyst activity. The structure changed from neatly stacked layers to a disorganized arrangement of the clay sheets resulting in threefold increase in the specific surface area. Furthermore, the combination of both micro- and mesoporous volume allowed easier access to the active sites as shown on Figure 1. Research on the source and nature of the acidity of Sn-MMT is still ongoing.



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## Ammonia Synthesis and catalyst poisoning: understanding the catalyst activity to improve the process

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The catalytic ammonia synthesis from H<sub>2</sub> and N<sub>2</sub> is one of the most important industrial reactions. The catalyst is made from iron oxide with few percent by weight of other oxides added as promoters. Despite the improvement made in the recent years the catalyst is still sensitive to the poison due to oxygenates compounds. The poisoning in ammonia synthesis catalysts is usually related to the adsorption of oxygen on the iron catalytic surface. The coverage of oxygen on the iron surface is dynamic and depends on the pressure, temperature and gas composition. The poisoning effect of oxygenates compounds (CO<sub>2</sub>, CO, O<sub>2</sub> and H<sub>2</sub>O) on the ammonia synthesis catalyst has been investigated in the last decades<sup>1</sup>.

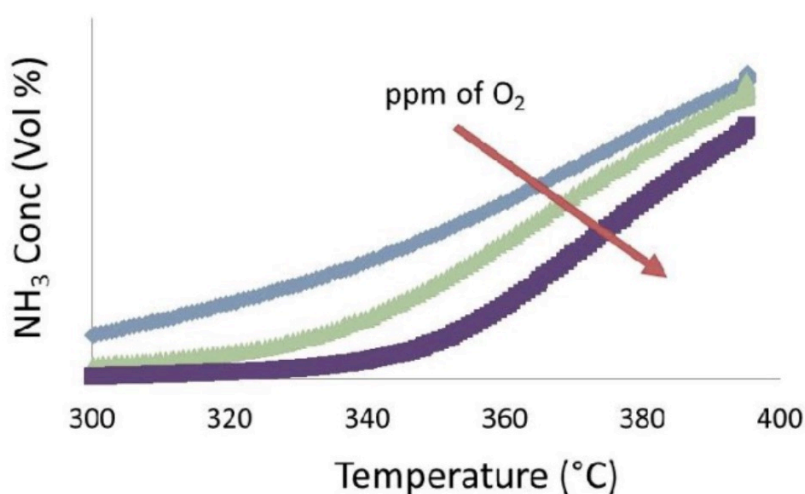


Fig. 1: Effect of different amount of O<sub>2</sub> on the ammonia synthesis catalyst

In normal industrial conditions, few ppm of oxygenates compounds can reach the ammonia synthesis reactor, and even if they are below 10 ppm they affect the iron catalyst life and performances. For the reasons mentioned above we have investigated the influence of a O<sub>2</sub>+H<sub>2</sub>O mixture on the ammonia synthesis catalyst to determine the extent of the poisoning in different reaction conditions. The scope of the work was to compare data from lab scale experiments with industrial reactors data to find correlations that can be used to predict catalyst life, reactor performances and how to operate in case of drastic poisoning in industrial reactors. The understanding of the chemistry behind the effect of few ppm of oxygenates compounds in industrial reactors, can reveal new insights on the ammonia synthesis reaction that will increase drastically the reactors' performances.

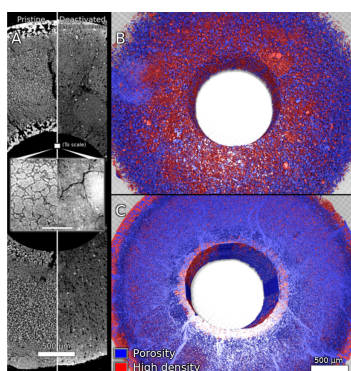
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## Multi-Scale Characterization and Porous Network Efficiency Analysis on VPO Catalytic Bodies

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The partial oxidation of butane into maleic anhydride is a chemical conversion process of industrial relevance. In this process vanadium phosphate catalysts are used to direct the reaction away from the full combustion of butane to the formation of maleic anhydride, which is a raw material in the manufacturing of unsaturated polyester resins, which are essential to the production of household and industrial plastics. These catalysts decrease in catalytic activity with time, necessitating their replacement. The mm-sized VPO catalyst pellets studied here contain catalytic reaction promoting bismuth particles ( $\varnothing$  60 nm). Their porous network consists of macro- (>50 nm) and mesopores (2-50 nm) [1, 2].



To get an understanding of the structure of these catalytic bodies, they were studied at different scales, using a variety of tomographic and 2D imaging techniques. Since the structure of these particles is very heterogeneous, selecting a small fraction of it would not contribute much to the understanding of the functionality of the entire pellet. The whole body of the pellets was scanned using state-of-the-art desktop X-ray tomography device with a  $\sim 4 \mu\text{m}$  resolution, an internal subvolume scanned with  $\sim 200 \text{ nm}$  resolution using holographic tomography at the ID16A beamline at the ESRF, and currently work is being done to achieve  $\sim 30 \text{ nm}$  resolution on these samples using ptychographic tomography at the cSAXS beamline at SLS, PSI. The porous network that was revealed by these methods was analyzed for efficiency, using the common network efficiency parameters - such procedure was not attempted in the field of heterogeneous catalysts' characterization before, to the best of our knowledge. The nano-structure is being analyzed using TEM, HR-XRD, and scanning micro-probe diffraction.

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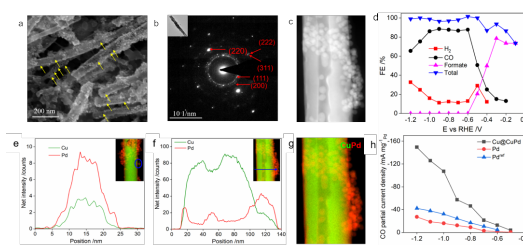


## Electrocatalytic CO<sub>2</sub> Reduction on Stable Cu@CuPd Core-shell Nanowires

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The highly selective and efficient electroreduction of CO<sub>2</sub> (CO<sub>2</sub>RR) toward value-added products crucially relies on the rational design of catalysts on various length scales. The fabrication of bimetallic nanostructures with hierarchical morphologies and defined elemental distributions can be considered as a highly promising approach to guide not only the reactivity and selectivity of the catalyst, but also to minimize the utilization of precious metals and to further improve the catalyst degradation behavior. Herein, we report on a novel synthesis strategy for optimized CO producing CO<sub>2</sub>RR catalysts that is based on a wet-chemical synthesis of Cu nanowires combined with a subsequent galvanic Cu/Pd displacement reaction. With this strategy, pristine Cu nanowires are transformed into [110]-oriented nano-wires with an outermost shell that is composed of a bimetallic CuPd alloy (Cu@CuPd) as evidenced by combined XPS, XRD analysis and energy dispersive X-ray (EDX) line-scanning/mapping (Fig. 1). Inspection by HR-SEM reveals diameters of these Cu@CuPd nanowires in the range of ~ 80 nm whereas their length is in the range of microns. The outermost surface of the Cu@CuPd nanowires is decorated by extra Pd-rich CuPd-NPs having diameters in the range of ~ 2 nm. In this study we demonstrate that the as-synthesized Cu@CuPd nano-wires outperform conventional Pd and Cu catalysts in the selective conversion of CO<sub>2</sub> into CO (Fig. 1d). The CO mass activity of the Cu@CuPd catalyst reaches 46.2 mA mg<sup>-1</sup><sub>Pd</sub> at -0.8 V vs RHE which three times higher than one of the most active Pd<sup>1</sup> catalyst reported so far (Fig. 1h). Furthermore, the Cu@CuPd catalyst shows superior durability properties. Due to the presence of Cu, irreversible CO poisoning of the Pd is prevented. Controllable fabrication of bimetallic core-shell electrocatalysts, particularly with the less-noble metal as the core, is a promising strategy to obtain efficient, selective, cost-effective and stable catalysts for electrochemical CO<sub>2</sub>RR.



**Figure 1** a, SEM image of carbon supported Cu@CuPd nanowires; b, SAED pattern of the Cu@CuPd nanowire shown in the inset; c, HAADF-STEM image of the Cu@CuPd nanowire; d, EDX line-scan profile acquired across a single particle shown in the blue cycle; e, EDX line-scan profile acquired across the blue arrow in the insert image; f, EDX map of the nanowire displayed in Figure 1c superimposing the Cu and Pd contributions.

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**Bulk and surface properties of Sr<sub>2</sub>TaO<sub>3</sub>N by density functional theory**M. Bouri<sup>1</sup>, U. Aschauer<sup>1\*</sup><sup>1</sup>Departement für Chemie und Biochemie, Universität

Photocatalytic water splitting is a clean and renewable process for H<sub>2</sub> production that can be used as an energy carrier in fuel-cell vehicles. However, the design of new materials with efficient photocatalytic properties is important to render this process economically viable. Perovskite oxides with layered structures are reported to be promising candidate materials for water-splitting catalysts [1]. Moreover, the substitution of oxygen with nitrogen in the perovskite structure leads to novel physical and chemical properties due to their difference in electronegativity [2]. Nevertheless, the electronic structure of such oxynitrides with layered perovskite structure as well as their catalytically active surface has not been studied thoroughly.

In this work, we perform density functional theory (DFT) calculations to investigate the structural and electronic features of Ruddlesden-Popper oxynitride Sr<sub>2</sub>TaO<sub>3</sub>N as well as its (001) and (100) surface. We show that the (001) TaON-terminated surface exhibits promising photocatalytic properties due to the suppression of electron-hole recombination by nitrogen-derived surface hole states.

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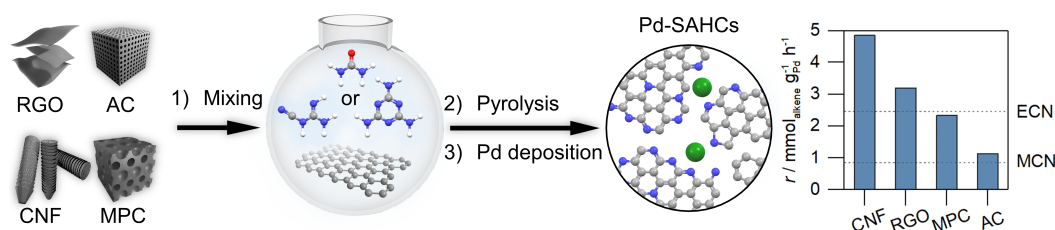
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## Design of nitrogen-doped carbon hosts for single-atom catalysts

S. Büchele<sup>1</sup>, Z. Chen<sup>1</sup>, S. Mitchell<sup>1</sup>, J. Pérez-Ramírez<sup>1\*</sup>

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The development of efficient single-atom heterogeneous catalysts (SAHC) has sparked significant enthusiasm worldwide, arising from the prospect of maximizing metal utilization and selectivity simultaneously. Carbon nitride has been shown to be highly effective in stabilizing atomically-dispersed metal species due its high concentration of surface nitrogen groups.<sup>1</sup> However, the tunability of the surface chemistry of this material and related reactivity of incorporated metals is somewhat limited. In contrast, nitrogen-doped carbons offer a broader scope due to the large number of methods for their synthesis and modification. Despite the great success in carbon-based SAHCs and their application in multiple highly relevant reactions, the understanding of the coordination sites remains vague.<sup>2</sup> Starting with carbon materials of distinct morphology (nanosheets, mesoporous, microporous, and nanofibers), here we compare effective ways to introduce nitrogen and the associated ability to stabilize palladium atoms (Figure 1). Surface functionalization is performed *via* the pyrolysis of carbon in the presence of nitrogen-containing molecules (dicyandiamide, melamine, urea) at varying temperature. The content and arrangement of the introduced nitrogen, and the associated metal speciation, heavily depend on the utilized dopant. Evaluation in the semi-hydrogenation of 2-methyl-3-butyn-2-ol shows that palladium single atoms on carbon supports can outperform carbon nitride based SAHCs (ECN/MCN),<sup>3</sup> enabling further improvement of the Pd coordination site. This study provides new mechanistic insights into the interaction between surface nitrogen functionalities and isolated palladium atoms and demonstrates the potential of a simple and scalable approach to develop SAHCs with tunable properties.



**Figure 1** Synthesis of atomically-dispersed Pd species on nitrogen-doped carbons derived from distinct carbon materials and catalytic evaluation in the semi-hydrogenation of 2-methyl-3-butyn-2-ol.

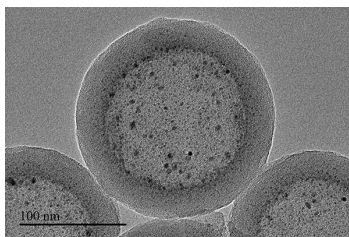
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**Selective Depolymerization of Lignin over Rh@HCS in Methanol**L. Chen<sup>1</sup>, A. P. van Muyden<sup>1</sup>, P. J. Dyson<sup>1</sup>, G. Laurency<sup>1</sup><sup>1</sup>EPF Lausanne

Since lignocellulose is renewable, sustainable and inedible, it may contribute to the substitution of fossil fuel if it can be selective degraded into several major products. In birch wood, 4-n-propanolsyringol unit contributes most to it.<sup>1</sup> These monomers can be used in resins production, and be acted as building block for aromatics chemicals production.<sup>2</sup>



Commercial catalysts are more widely used in sawdust conversion, for example Pd/C,<sup>3</sup> Ru/C,<sup>2</sup> Pt/C,<sup>4</sup> Raney@Ni,<sup>5</sup> while Rh based catalyst is still under unexplored. The Rh@HCS, shown in Fig. 1, is well dispersed Rh nanoparticles on the hollow carbon sphere (HCS). With methanol, the solvolysis contributes to the C-O bonds, and the yield of monolignols is 47% with 50% selectivity of 4-n-propanolsyringol. The effect of solvents, temperature, catalysts, and acidity/based additives were studied and the impact on the yield of monolignols and product selectivity was investigated, showing that this catalytic biorefinery approach may be feasible in the near future.

**Acknowledgements**

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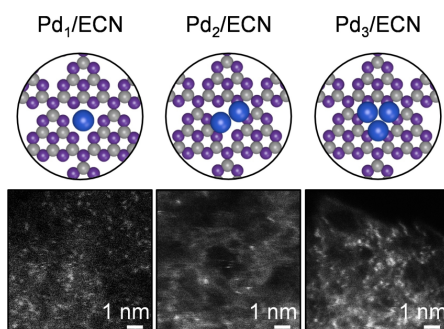
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**Stabilization of Pd<sub>n</sub> catalysts (n = 1-3) on carbon nitride and nuclearity dependence in hydrogenations and C-C couplings**

Z. Chen<sup>1</sup>, E. Vorobyeva<sup>1</sup>, S. Mitchell<sup>1</sup>, E. Fako<sup>2</sup>, G. Vilé<sup>3</sup>, S. M. Collins<sup>4</sup>, P. A. Midgeley<sup>4</sup>, O. V. Safonova<sup>5</sup>, N. López<sup>2</sup>, J. Pérez-Ramírez<sup>1\*</sup>

<sup>1</sup>D-CHAB, ETH Zurich, <sup>2</sup>ICIQ, Spain, <sup>3</sup>Idorsia Pharmaceuticals Ltd., <sup>4</sup>University of Cambridge, <sup>5</sup>Paul Scherrer Institute

Solids integrating atomically-dispersed metals receive considerable attention aiming to combine the excellent metal utilization attained by homogeneous catalysts with the robustness and facile recovery offered by traditional nanoparticle-based heterogeneous catalysts.<sup>1</sup> In particular, single-atom heterogeneous catalysts represent a geometric limit in terms of active site size, whereas larger ensembles may be more effective in some reactions. However, the controllable synthesis of supported multi-atom ensembles is highly challenging due to the tendency of nanoparticle aggregation. Here we report a facile bottom-up strategy to introduce three distinct palladium ensembles on exfoliated carbon nitride. The electronic and geometric properties are studied by X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, and aberration-corrected scanning transmission electron microscopy, showing a lower degree of oxidation and increased coordination number upon increasing the ensemble size. The nuclearity dependence of Pd<sub>1-3</sub> ensembles is evaluated in selective hydrogenation and C-C coupling reactions evidencing distinct activity trends, which is further supported by Density Functional Theory. The complexity of the nuclearity dependency demonstrates the critical role of designing metal ensembles to reach the fullest potential of atomically-dispersed catalysts.



**Figure 1** Development of Pd<sub>n</sub> catalysts based on carbon nitride (ECN).

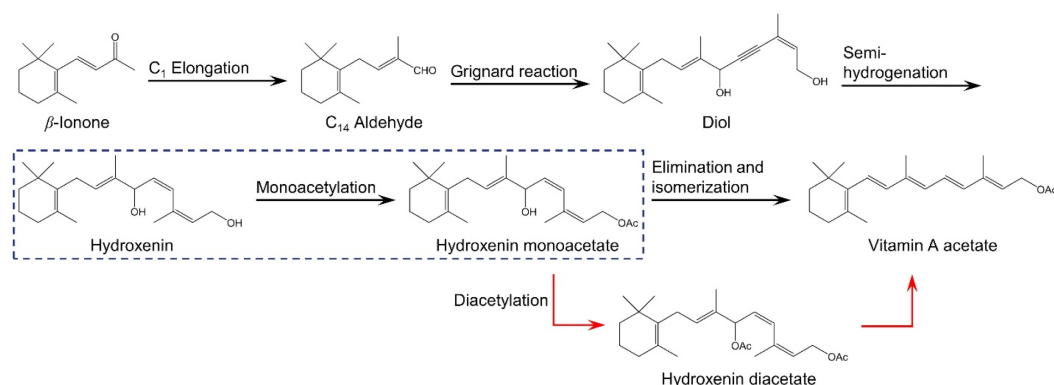
[1] J. Liu, *ACS Catal.* **2017**, 7, 34; G. Vilé, D. Albani, M. Nachtegaal, Z. Chen, D. Dontsova, M. Antonietti, N. López, J. Pérez-Ramírez, *Angew. Chem. Int. Ed.* **2015**, 54, 11265; Z. Chen, S. Mitchell, E. Vorobyeva, R.K. Leary, R. Hauert, T. Furnival, Q.M. Ramasse, J.M. Thomas, P.A. Midgley, D. Dontsova, M. Antonietti, S. Pogodin, N. López, J. Pérez-Ramírez, *Adv. Funct. Mater.* **2017**, 27, 1605785; E. Vorobyeva, Z. Chen, S. Mitchell, R. K. Leary, P.A. Midgley, J.M. Thomas, R. Hauert, E. Fako, N. López, J. Pérez-Ramírez, *J. Mater. Chem. A* **2017**, 5, 16393.

## Design of solid bases for the sustainable synthesis of a vitamin A intermediate

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Continued economic growth will contribute to increasing demand for vitamin A, which is an essential micronutrient for many biological functions including growth, immunity, vision, and fertility [1]. The production of the more stable acetate derivative is still characterized by the use of stoichiometric amounts of soluble reagents, requiring costly separation and treatment steps. For instance, the monoacetylation of hydroxenin, a key intermediate step in the current manufacturing route, relies on the addition of an organic base to achieve high selectivity (**Figure 1**). Although the use of solid alternatives may improve recyclability and waste minimization, their application in the manufacture of fine chemicals remains limited due to the challenges associated with identifying suitable materials that meet the stringent criteria for high product purity [2]. This work targets the development of solid bases for the synthesis of an industrially relevant vitamin A intermediate. To guide the design, it was first necessary to identify the role of the soluble reagents in the acetylation of hydroxenin. Based on these insights, common basic materials were assessed for their performance in the monoacetylation reaction. Once promising candidates were identified, both the activity and product selectivity were further enhanced through optimization of surface area, pore volume, and basic site concentration by tuning the material's composition and treatment conditions. The resulting process using solid bases showed prolonged stability of the most active material over several consecutive reactions without any significant loss of activity.



**Figure 1:** The synthesis of vitamin A acetate developed by Hoffmann-La Roche starting from  $\beta$ -ionone.[1] The boxed reaction step is investigated in this study.

[1] M. Eggersdorfer, D. Laudert, U. Létinois, T. McClymont, J. Medlock, T. Netscher, W. Bonrath, *Angew. Chem. Int. Ed.* 2012, **51**, 12960-12990.

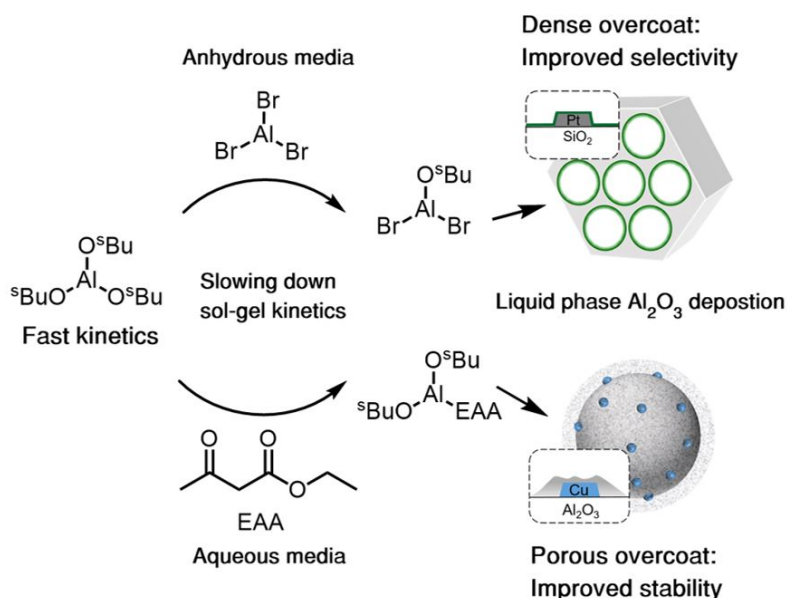
[2] A. L. de Lima, C. M. Ronconi, C. J. A. Mota, *Catal. Sci. Technol.* 2016, **6**, 2877-2891.

## Slowing the Kinetics of Alumina Sol-gel Chemistry for Controlled Catalyst Overcoating and Improved Catalyst Stability and Selectivity

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Catalyst overcoating is an emerging approach to engineer controlled surface functionalities on supported metal catalyst and improve catalyst selectivity and durability. Alumina deposition on high surface area material by sol-gel chemistry has traditionally been difficult to control due to the fast hydrolysis kinetics of aluminum-alkoxide precursors. Here, we adapt sol-gel chemistry methods to slow down these kinetics. We report that, using different approaches to slow the kinetics of liquid phase sol-gel methods, we can deposit nanometer-scale alumina overcoats with similar chemical properties but distinct physical textures onto high surface area substrates. Importantly, the alumina overcoats are comparable in conformality to the overcoats prepared from atomic layer deposition even on high surface area substrates, as shown by imaging and infrared spectroscopy. Our strategy relies on regulating the hydrolysis/condensation kinetics of  $\text{Al}(\text{sBuO})_3$  by adding a chelating agent or using non-hydrolytic sol-gel chemistry. With chelation chemistry, a mild method that is compatible with deposition over supported base metal catalysts, a conformal yet porous overcoat leads to a highly sintering-resistant Cu catalyst for liquid-phase furfural hydrogenation. With the non-hydrolytic sol-gel route, a denser  $\text{Al}_2\text{O}_3$  overcoat can be deposited to create a high density of Lewis acid-metal interface sites over Pt/SBA-15. This overcoated Pt/SBA-15 has a substantially increased hydrodeoxygenation activity for the conversion of lignin-derived 4-propylguaiaicol into propylcyclohexane with up to 87% selectivity.



## Beyond Copper in CO<sub>2</sub> Electrolysis: Effective Hydrocarbon Production on Silver Nano-Foam Catalysts

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<sup>1</sup>University of Bern, Switzerland

Novel Ag foam catalysts have been developed for the electrochemical CO<sub>2</sub> reduction reaction (ec-CO<sub>2</sub>RR) based on a concerted additive- and template-assisted metal deposition process (Fig.1). In aqueous media these Ag foams show superior activity and selectivity towards CO production at low and moderate overpotentials. Faradaic efficiencies for CO (FE<sub>CO</sub>) never fell below 90% within an extremely broad potential window of ~900 mV. At potentials < -1.1 V vs RHE the FE<sub>H<sub>2</sub></sub> values significantly increase at the expense of FE<sub>CO</sub>. Superimposed on this anti-correlated change in the CO and H<sub>2</sub> efficiencies is the rise in the CH<sub>4</sub> efficiency to the maximum of remarkable FE<sub>CH<sub>4</sub></sub> = 51% at -1.5 V vs RHE. As a minor side-product, even C-C coupled ethylene could be detected reaching a maximum Faradaic efficiency of FE<sub>C<sub>2</sub>H<sub>4</sub></sub> = 8.6% at -1.5 V vs RHE. This study reports on the first ec-CO<sub>2</sub>RR catalyst beyond copper that demonstrates exceptionally high selectivity towards hydrocarbon formation reaching a maximum of amazing ~60% at -1.5 V vs RHE. Experimental observations presented herein strongly suggest that this novel Ag foam catalyst shares in part mechanistic features with common Cu catalysts in terms of ec-CO<sub>2</sub>RR product selectivity and catalyst degradation behavior.

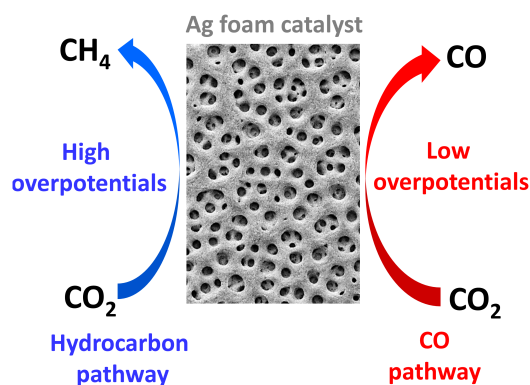


Fig.1. SEM images of hydrogen template assisted electrochemical deposition Ag foam nano-structured

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[2] H. C. Shin, J. Dong, M. L. Liu, Adv. Mater. 2004, 16 (3), 237–240

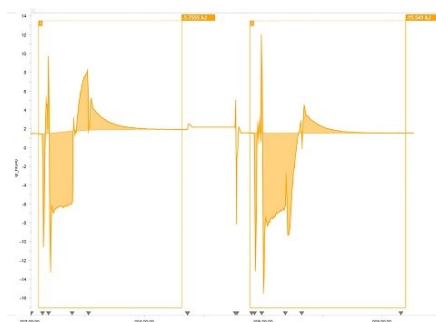


**A Viable Hydrogen-Storage System: Towards the “Formic Acid Battery”**C. Fink<sup>1</sup>, G. Laurency<sup>1\*</sup><sup>1</sup>EPF Lausanne

Hydrogen storage via homogeneously catalyzed carbon dioxide (CO<sub>2</sub>) reduction to formic acid (FA) and the reverse reaction to liberate hydrogen via FA dehydrogenation is a promising technology for a future hydrogen economy.<sup>[1]</sup> Here, we want to highlight vital steps which lead to the development of an FA powered electricity generator (prototype). At the current level of technology, the search for improved catalysts plays a central role.<sup>[2]</sup> Therefore we studied a series of iridium complexes, which are part of a larger group of structures, known to be able catalysts for FA dehydrogenation. Our contribution was the systematic examination of small diamine ligands to evaluate steric and electronic effects.<sup>[3]</sup> The survey included NMR spectroscopic measurements and the determination of the activation energy, E<sub>a</sub>.

In another work, we looked into solvent-FA interactions to elucidate how different solvents and additives stabilize formic acid in case of CO<sub>2</sub> hydrogenation. DMSO<sup>[4]</sup> and water were considered as more relevant solvents and therefore carefully examined. The results are considered as needed tools for engineers to design hydrogen storage devices. The methods we deployed were heat-flow calorimetry, multinuclear NMR -and FTIR spectroscopy as well as computational methods to generate a compressive model of occurring intermediates and species.<sup>[5]</sup> FA dehydrogenation is volunteer reaction despite being endothermic. High-pressure reaction calorimetry revealed to which extent FA dehydrogenation is endothermic under experimental conditions and enabled us to quantify the energy required to dehydrogenate one mole of FA.

**Acknowledgement:** EPFL and SCCER are thanked for financial support.



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- [4] S. Moret, P. J. Dyson, G. Laurency, *Nat. Commun.* **2014**, *5*.
- [5] C. Fink, S. Katsyuba, G. Laurency, *PCCP* **2016**, *18*, 10764-10773.

## **Pd nanoparticles solid-liquid interface study during liquid phase selective hydrogenation by combined XAS and ATR-IR**

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<sup>1</sup>Paul Scherrer Institut, <sup>2</sup>EPFL

Hydrogenation reactions occupy an important place in the realm of catalysis with various functional groups such as double and triple bonds and aldehydes among others which can undergo hydrogenation to produce diverse intermediates and fine chemicals [1]. In the fine chemical industry, these reactions are often performed in liquid phase due to the thermal stability and sensitivity of the compounds. Hydrogenation of furfural in liquid phase was chosen as a model hydrogenation reaction because the conversion and product selectivity are sensitive to both temperature of reaction and solvent [2]. Our aim is to understand the composition of the solid-liquid interface and how solvents and reaction conditions influence on the conversion and the product selectivity of a specific metal. For this purpose, we used X-ray absorption spectroscopy (XAS) to monitor the oxidation state and local environment of Pd during reduction and reaction in the liquid phase (5 bar). Infrared spectroscopy in the attenuated total reflectance mode (ATR-IR) was exploited to follow the nature of the adsorbed species under similar reaction conditions. A commercial reduced 5 wt.% Pd/Al<sub>2</sub>O<sub>3</sub> was used to perform hydrogenation of furfural in three solvents (isopropanol, cyclohexane and toluene). The Pd nanoparticles were partially oxidized by storage in air but were fully reduced at 125°C before changing to the hydrogenation reaction conditions. During reduction, the XANES features of Pd metal shifted to lower energy, which together with the increase of the Pd-Pd bond distance from 2.74 Å to 2.81 Å are signatures of the formation of hydrides on the Pd surface. Admittance of the hydrogenation mixture containing furfural consumed these species. The intensity of the XANES features and the Pd-Pd bond distance after reduction of Pd were different depending on the solvent suggesting that the hydrogen coverage is governed by the selected solvent. ATR-IR spectroscopy allowed monitoring the adsorption and reaction of furfural at the surface of the catalyst when admitting the furfural solution to the catalyst after reduction. The observation of adsorbed CO on Pd metal was related to the formation of furan, which is the major product of furfural decarbonylation in cyclohexane and isopropanol. Lower CO signals together with the absence of a-top CO were observed in toluene, in which solvent, furfuryl alcohol is the major product, indicating that hydrogenation of furfural is taking place on specific sites.

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## High Performance Electrochemical Water Oxidation Using Manganese Oxide-Based Electrodes

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Water electrolysis into H<sub>2</sub> and O<sub>2</sub> is an ideal approach for sustainable and large-scale production of pure hydrogen. For this purpose, electricity generated from renewable energy sources such as solar and wind can be effectively utilized. However, the main challenge in water splitting is oxidation half-reaction involving multi-electron transfer due to its high thermodynamic potential and kinetic barrier. Hence, the development of high performance water oxidizing catalysts, which can overcome these limitations, is of utmost interest. In this work, a series of manganese oxide/FTO electrodes were fabricated and utilized for water oxidation reaction at pH= 7. The fabricated electrodes were calcined at different temperatures and the differences in water oxidation ability among these catalysts were probed using X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The most active catalyst showed a stable current density of 1.0 mA.cm<sup>-2</sup> at an over potential of 480 mV for more than 3 days. Even greater current densities of 9 and 13 mA.cm<sup>-2</sup> have been achieved at 1.4 and 1.5 V (vs. Ag|AgCl), respectively.

**Ionic Liquid Catalysts and the N-Formylation of Amines with CO<sub>2</sub>; Scope, Reactivity, Mechanism and the Chemical Equilibria Involved**

M. Hulla<sup>1</sup>, F. Bobbink<sup>1</sup>, S. M. Chamam<sup>1</sup>, P. J. Dyson<sup>1\*</sup>, G. Laurenczy<sup>1\*</sup>

<sup>1</sup>EPF Lausanne

Carbon dioxide is cheap, non-toxic and renewable (C1) building block for chemical synthesis. However, CO<sub>2</sub> is thermodynamically and kinetically stable, posing a challenge to its efficient use in the production of commodity chemicals. Ionic liquids, simple organic salts, are efficient catalysts for the N-formylation of amines with CO<sub>2</sub> and hydrosilane reducing agents. Optimization of the ionic liquid composition and functionality allows the N-formylation reaction to proceed at ambient conditions with almost unlimited substrate scope. Investigation into the reaction mechanism revealed a series of intricate reaction equilibria which, when controlled, allow the synthesis of N-Methyl amines and aminated from the same starting materials.

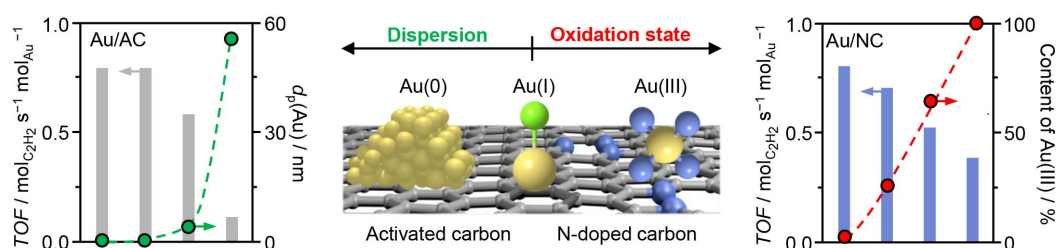
Martin Hulla, Felix D. Bobbink, Shoubhik Das and Paul J. Dyson, *ChemCatChem*, **2016**, 8, 3338-3342

## Controlling the speciation and reactivity of carbon-supported gold nanostructures in catalyzed acetylene hydrochlorination

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<sup>1</sup>D-CHAB, ETH Zurich, <sup>2</sup>ICIQ, Spain

Carbon-supported gold nanostructures have the potential to ultimately replace the highly toxic mercuric chloride-based catalyst in acetylene hydrochlorination, a key technology for the sustainable manufacture of polyvinyl chloride.<sup>1</sup> However, the wide implementation of gold catalysts is still hindered by their limited durability under practically relevant reaction conditions. To enable the rational design of stable gold nanostructures, it is essential to find the most active site among the variety of candidates that have been identified to date, including nanoparticles, clusters, and recently also single atoms.<sup>2</sup> Here, we unravel the activity hierarchy with a systematic evaluation of the metal dispersion and oxidation state as descriptors for gold-based catalysts in acetylene hydrochlorination, using a platform of supported nanostructures ranging from single atoms of tunable oxidation state to metallic nanoparticles at a fixed loading. Our approach takes advantage of the fundamentally different behavior of gold atoms hosted on activated carbon (AC) in comparison to polyaniline-derived N-doped carbon (NC). While on AC particle aggregation occurs progressively above 473 K, on NC gold single atoms exhibit outstanding thermal stability under reaction conditions and during thermal treatment up to 1073 K, as confirmed by aberration corrected transmission electron microscopy and extended X-ray absorption fine structure spectroscopy. With an integrated approach combining steady-state experiments, density functional theory, and transient mechanistic studies we show and rationalize the superior performance of atomically dispersed Au(I)Cl species irrespective of the choice of carrier (Figure 1). In relation to the structure of the active site and the corresponding reaction mechanism, we discuss perspectives for the development of highly active and stable hydrochlorination catalysts.



**Figure 1** The gold particle size ( $d_p$ ) and oxidation state determine the catalytic performance of gold-based catalysts in acetylene hydrochlorination, expressed as the turnover frequency (TOF).

[1] R. Lin, A. P. Amrute, J. Pérez-Ramírez, *Chem. Rev.* **2017**, 117, 4182.

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## Unprecedented methane to methanol conversion on Cu-zeolites: Copper concentration dependent activity in zeolite omega

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<sup>1</sup>ETH Zürich, <sup>2</sup>Paul Scherrer Institut

Directly converting methane to methanol is a proposed route for utilization of methane that is otherwise wasted through flaring<sup>1,2</sup>. Copper exchanged omega (Cu-MAZ) zeolite is one of the most promising materials to date for this process<sup>3</sup>. Through improvement in the hydrothermal synthesis, we can produce pure and uniform MAZ crystallites. For the stepwise conversion of methane to methanol<sup>4</sup>, this Cu-MAZ yields 150  $\mu\text{mol}$  methanol/gram-zeolite under 1 bar methane and as high as 200  $\mu\text{mol}$  methanol/gram-zeolite at 30 bar (Figure 1), the highest ever reported.

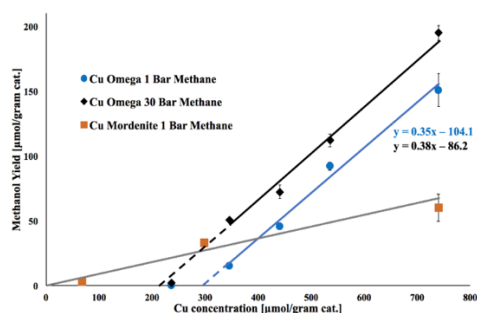


Figure 1: Methanol yield as a function of copper load for Cu-omega and Cu-mordenite

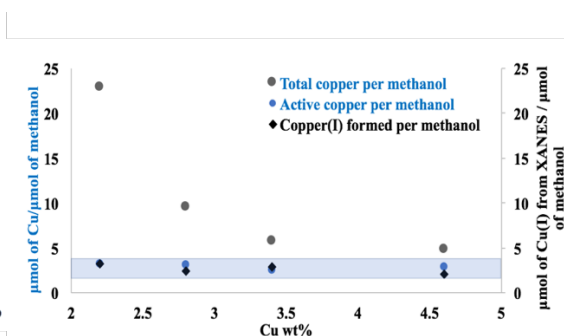


Figure 2: (Right Axis) Ratio of  $\mu\text{mol}$  of Cu(I) formed during reaction by the  $\mu\text{mol}$  of methanol formed. (Left Axis) Ratio of  $\mu\text{mol}$  of total and calculated active copper to  $\mu\text{mol}$  of methanol

Furthermore, by evaluating the methanol yield at different copper loadings, the methanol yield shows a distinct dependency on the copper concentration. At a low concentration of copper, Cu-MAZ is inactive. Once a minimum copper concentration is reached, the methanol yield increases at a rate of 2.8 mol-Cu/mol-MeOH for 1 bar methane and 2.6 mol-Cu/mol-MeOH for 30 bar. To characterize the inactive and active phases, we have employed a series of synchrotron based techniques (in-situ diffraction and x-ray absorption). The combination of the high yields and better understanding of the active site represents a step forward for achieving better performing materials for methane to methanol conversion.

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## Ruthenium catalyst for dry biomass derived CO methanation in the presence of sulfur poisons

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<sup>1</sup>Paul Scherrer Institute, <sup>2</sup>ETH Zürich

The process of methane production from dry biomass, called wood-to-Synthetic Natural Gas (SNG), consists of 4 main steps: biomass gasification, a purification step to remove from syngas the catalyst poisons such as H<sub>2</sub>S, COS and C<sub>4</sub>H<sub>4</sub>S using “cold” gas cleaning technologies, methanation and upgrading to remove H<sub>2</sub>O and CO<sub>2</sub>.<sup>1</sup> To make wood derived SNG cost-competitive, a process intensification that would allow methanation directly from biogas containing sulfur poisons would be desired.<sup>2</sup> In that context, the development of ruthenium-based catalysts, which can be regenerated under oxidizing atmosphere after sulfur poisoning, is explored and discussed (Fig. 1).

While Ru nanoparticles supported on alumina deactivate very fast due to irreversible sulfur poisoning of the support (formation of aluminium sulfate), the corresponding silica-supported Ru catalyst show promising catalyst performance, because silica show a lower sulfur storage by comparison with alumina as shown by MS, S K-edge XAS and DRIFTS. However, a complete recovery of the catalytic activity cannot be achieved after regeneration. In this presentation, we show how varying the parameters of the oxidative regeneration step, such as temperature, O<sub>2</sub> partial pressure and treatment duration, affects the recovery of the catalytic activity.

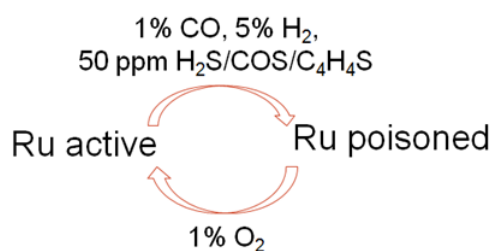


Fig. 1: Poisoning-regeneration cycle

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- [2] C. F. J. König et al., *Catalysis Today*, **2014**, 229, 56 – 63

## Selective Methanol Synthesis by Zirconium Surface Sites in Silica-supported Cu Nanoparticles: Synthesis and Spectroscopy

E. Lam<sup>1</sup>, K. Larmier<sup>1</sup>, P. Wolf<sup>1</sup>, S. Tada<sup>1</sup>, O. V. Safonova<sup>2</sup>, C. Copéret<sup>1\*</sup>

<sup>1</sup>ETH Zürich, <sup>2</sup>Paul Scherrer Institute

The increasing amount of carbon dioxide (CO<sub>2</sub>) in the atmosphere has a direct impact on global warming and is a direct consequence of the use of fossil fuels as our main energy sources. One way to mitigate its increase is to incorporate CO<sub>2</sub> in a carbon-energy-cycle and to transform it into more valuable compounds such as methanol following the concept of the “methanol economy”. [1] The hydrogenation of CO<sub>2</sub> to methanol is possible with Cu-based catalysts. Promising catalytic efficacy (methanol activity and selectivity) can be reached by choosing specific metal oxide supports for Cu such as zirconia, while silica as a support favors the competing reverse water-gas-shift reaction (RWGS) forming CO and H<sub>2</sub>O instead. [2] We have recently shown that the improved activity and selectivity in zirconia-supported Cu nanoparticles is due to the favored formation of CH<sub>3</sub>OH at the interface between copper and zirconia. [3] In particular, it has shown that the role of Zr Lewis acid sites at the surface of zirconia and in close proximity to the Cu nanoparticles, is to facilitate the formation of formate and their conversion into methoxy species.

We reasoned that it is possible to tailor the activity of CO<sub>2</sub> hydrogenation catalysts by selectively incorporating Zr(IV) species at the interface with the Cu particles. We thus used a surface organometallic chemistry (SOMC) combined with a thermolytic precursor (TMP) approach to generate first well-defined isolated Zr(IV) surface sites on silica and then grow small and narrowly distributed Cu nanoparticles by grafting a Cu molecular precursor followed by a treatment under H<sub>2</sub>. This material demonstrates promotional effect in CO<sub>2</sub> hydrogenation at 230 °C and 25 bars, providing increased activity and selectivity towards CH<sub>3</sub>OH formation in comparison to benchmark Cu/SiO<sub>2</sub> catalysts. In addition, thanks to the presence of isolated Zr(IV) surface sites it is possible to monitor the coordination environment and oxidation state of zirconium using in-situ and ex-situ X-ray absorption, NMR and IR spectroscopy. This study allows rationalizing and understanding on a molecular level the role of oxide supports in catalysis and provides guidelines to improve catalyst design.

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## Cheap and upscalable process for atomic layer deposition on powder through stoichiometric grafting in solution.

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<sup>1</sup>EPF Lausanne

Atomic layer deposition (ALD) is an efficient method for thin layer deposition based on alternate exposure of gaseous metal precursor and oxygen source. First designed for film deposition on wafers, there is now a growing interest in ALD for tuning heterogeneous catalyst surface properties. For instance, great improvement in catalyst stability has been achieved through deposition of alumina over catalysts in the fields of biomass conversion<sup>1</sup> and methane activation<sup>2</sup>. Unfortunately, the high cost of equipment for deposition on powder and over consumption of expensive chemicals hinder the generalization of this technic in academic research and industry.

In this work, we designed a cheaper and upscalable process for atomic layer deposition on powder that required only standard inorganic chemistry equipment. The deposition follow the same surfaces reaction as ALD but with a control on stoichiometry, sparing time consuming purges and avoiding the waste of unreacted precursors. Beyond protective metal oxide deposition, our technic also open the door to multispecies grafting with controlled proximity allowing pairing or isolation of active sites.

As a proof of concept, alumina was deposited, from alkyl aluminum and water injections, on dispersed oxides. Influence of the support, the solvent and the precursor size on the grafting and cycling were assessed in order to demonstrate the flexibility of the method and to prepare the ground for a more accessible atomic layer deposition.

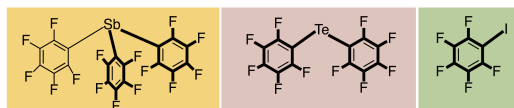
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**$\sigma$ -hole Interactions in Catalysis and Anion Transport**L. M. Lee<sup>1</sup>, S. Benz<sup>1</sup>, S. Matile<sup>1\*</sup><sup>1</sup>Department of Organic Chemistry, University of Geneva

The conditions that lead to the formation of  $\sigma$ -hole interactions constitute an appealing alternative to hydrogen bonding for the construction of supramolecular structures. In particular, halogen bonding has received a considerable attention due to their remarkable directionality and stability.<sup>1</sup>  $\sigma$ -hole interactions bearing other main group elements such as tetrels, chalcogens, and pnictogens have also been recognized. In all cases, the interaction stems from a combination of covalent, electrostatic and dispersion forces.

In this presentation, simple pentafluorophenyl derivatives containing group 15-17 elements have been explored. We show that  $\sigma$ -hole interactions are capable of halide binding catalysis<sup>2,3</sup> and anion transport across lipid bilayers. The efficiency is directly correlated with the depth of the  $\sigma$  holes of the main group element.



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## Understanding the functionality of molecular cocatalysts on hematite photoanode for water oxidation

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Photoelectrochemical water splitting is one of the most promising approaches for sustainable energy supply, and the development of efficient photoanode for water oxidation is a crucial technical challenge.[1] Many previous studies have shown that surface cocatalysts modification could significantly lower down the photocatalytic onset potential and thus provide higher photocurrent output. However, due to the multiple competing underlying processes, the role of these surface loaded cocatalysts is still not clear. Different mechanisms (passivation layer, formation of heterogeneous junction, hole accumulation and catalytic center) have been proposed based on observations probed by different techniques.[2] Here, we select a well-defined molecular cubane cocatalyst and the most-studied hematite photoanode as model system. Analysis of intensity modulated photocurrent transient spectra analysis indicates that the cocatalysts functionality is transforming, from mostly hole collectors to catalytic centers as the applied bias increases. This interesting dynamic functionality could also be observed using intensity modulated photoelectrochemical impedance spectra. Importantly, the observed phenomenon could be repeated by other molecular and particular cocatalysts. We believe this study could promote future understanding and design efficient cocatalyzed photoelectrode for wide range of applications.

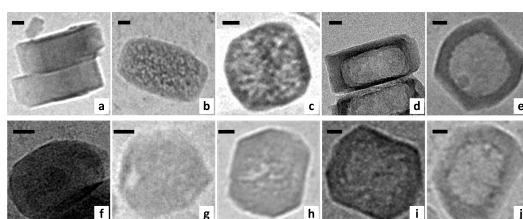
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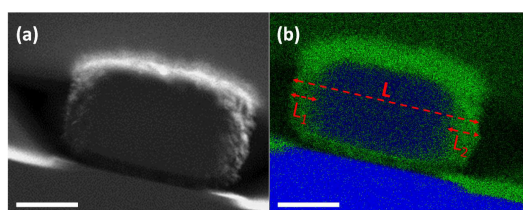
**Pore Formation in ZSM-5 Zeolites, a Transmission Electron Microscopy Study**T. Li<sup>1</sup>, J. A. van Bokhoven<sup>1,2\*</sup>

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A synthesis inherent inhomogeneity in aluminum distribution, Al-rich particle shell, allows the preparation of mesoporous or hollow ZSM-5 zeolites by simple base leaching. Understanding pore formation and the origin of this core-shell structure is essential for the design of better catalysts or particle hosts. Using transmission electron microscopy (TEM) to analyze ZSM-5 zeolite crystals leached for increasing periods of time, may not capture the details of the pore formation process, as leaching is usually followed by solid-liquid separation, drying and calcination. In contrast, cryo-TEM analysis, which involves the vitrification/ examination of the reaction slurry itself, can capture the process in its natural state.



Interestingly, although pore formation commenced throughout the whole Al-poor core, the mesopores of larger size firstly formed in an area close to the rim, suggesting a lower stability in this area. We have found that the boundary between the Al-rich and the Al-poor parts of the individual crystals is exactly the region where such pores are formed. The reason may be the strain in that area where two parts of the crystal with slightly different bond distances and angles – due to the different aluminum content – meet. The eventual preservation of the shell is mainly due to a higher concentration of aluminum of the rim locally. The negative charge of the  $\text{AlO}_4^-$  tetrahedra makes the rim more resistant to hydrolysis compared to the core. Therefore, the core-shell structure is formed by the selective removal of the silicon-rich inner part.



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## Influence of Synthesis Parameter in Microwave-HT Preparation of $\text{Co}_3\text{O}_4$ for Water Oxidation Catalysis

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Artificial photosynthesis offers a promising route towards renewable energy technologies. With sunlight, water is split into oxygen and hydrogen, which is storable or can be further converted into more convenient compounds. The main challenge of this method still remains the four electron transfer process of the water oxidation. Therefore the development of efficient, stable and economic water oxidation catalysts (WOC's) is required. In this context, spinel-type  $\text{Co}_3\text{O}_4$  has been attracting strong research interest as a low-cost and robust WOC<sup>1,2,3</sup>. While  $\text{Co}_3\text{O}_4$  is already a well-known catalyst for water oxidation, the parameters used during the synthesis methods and their influence on the crystallinity, morphology, Co(II)/Co(III) ratio and structure of the material still needs some more investigation<sup>4,5</sup>. Here, we study the effects of different synthesis parameters on the properties of the resulting material and tested it for water oxidation by the well-known photocatalytic  $\text{Ru}(\text{bpy})_3\text{-Na}_2\text{S}_2\text{O}_8$  protocol, measuring oxygen with GC of the headspace or by LDO in solution and then also by electrocatalytic LSV measurements with the catalyst fixed on FTO electrodes.

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## Uncovering the Interfacial Carrier Dynamics of CuInGaS<sub>2</sub> Photocathodes during Hydrogen Production

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Photoelectrochemical (PEC) water splitting is emerging as a solid platform that could sustain a carbon-free hydrogen community. Among the different photoactive materials that could integrate a PEC device for overall water splitting, the group of I-III-VI<sub>2</sub> semiconductors composed of CuIn<sub>x</sub>Ga<sub>1-x</sub>S<sub>2</sub> (CIGS) is drawing increasing attention as photocathode materials owing to their outstanding optoelectronic properties and tunable band gap. However, to cross the chasm to commercialization, two main issues are ambushing. First, conventional vacuum-based method (e.g. co-evaporate, co-sputter) limits the large-scale production. Second, this type of material generally needs overlayers/catalyst to perform hydrogen evolution reaction (HER).

Recently, an all-solution-processed CIGS photocathode demonstrated outstanding photoelectrocatalytic performance, even at its bare state.<sup>1</sup> Although the photocurrent onset is still far below the flat-band potential, this breakthrough offers an elegant solution for cost-effective solar fuel production.<sup>2</sup> Motivated by its splendid intrinsic catalytic properties and unsatisfactory photovoltage, we deployed three complementary *in situ* spectroelectrochemical techniques viz. photoelectrochemical impedance spectroscopy (PEIS), intensity-modulated photocurrent spectroscopy (IMPS) and *in situ* Raman spectroscopy to find out the reason for the limited photovoltage of this material. The new insights gained into the characteristics of the semiconductor-liquid junction (SCLJ) offer unprecedented information on the interfacial carrier dynamics (e.g. surface states, charge transfer/recombination kinetics and catalytic active sites) on this type of materials. Our results provide a closer look at the SCLJ and build the fundamental understanding for not only shift the onset potential but also further increase the PEC performance.

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**CO<sub>2</sub> Hydrogenation to Formate with Immobilized Ru-Catalysts based on Hybrid Organo-Silica Mesostructured Materials**H. Lo<sup>1</sup>, C. Copéret<sup>1\*</sup><sup>1</sup>Department of Chemistry and Applied Biosciences, E

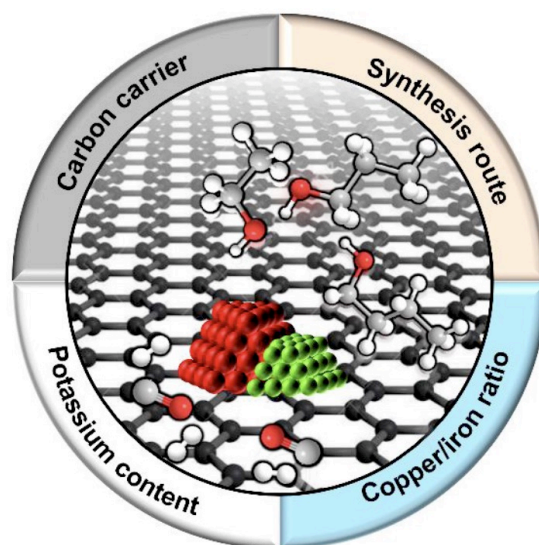
Formic acid, one of the CO<sub>2</sub> hydrogenation derivatives, is an efficient hydrogen carrier and has great potential to be applied in fuel cells.[1] Homogeneous transition metal catalysts have been developed to convert CO<sub>2</sub> to formic acid/formate in batch reactors, but the use of heterogeneous catalysts, which are more favored in industrial processes due to their practicality, is still sparse. In this work, we successfully synthesized an immobilized molecularly defined pincer-type N-heterocyclic carbene ruthenium complex supported on an organo-silica hybrid material, and evaluated its catalytic activity for CO<sub>2</sub> hydrogenation to a formic acid derivative. The activity of our supported catalyst to convert CO<sub>2</sub> to formate is similar to its homogeneous counterpart in terms of turnover number.[2] Our work shows the concept of immobilizing efficient homogeneous catalysts on the silica supports is totally feasible.

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**Higher alcohols synthesis over carbon-supported and K-promoted copper-iron catalysts**H. T. Luk<sup>1</sup>, C. Mondelli<sup>1</sup>, S. Mitchell<sup>1</sup>, S. Siol<sup>2</sup>, J. A. Stewart<sup>3</sup>, D. Curulla Ferré<sup>3</sup>, J. Pérez-Ramírez<sup>1\*</sup><sup>1</sup>ETH Zurich, <sup>2</sup>EMPA, <sup>3</sup>TOTAL Research & Technology Feluy

Higher alcohols have a broad range of applications in the chemical and energy industries. Nowadays, their production primarily relies on sugar fermentation and alkene hydration, but these processes suffer from either a high energy input for product separation or low single-pass conversion. The direct preparation from synthesis gas is regarded as a more economical and environmentally friendly alternative, which may also facilitate a wider exploitation of unconventional and renewable resources. Still, the identification of efficient catalysts, which combine C–C coupling and CO hydrogenation activities, remains a key challenge in catalysis research.<sup>1</sup> CuFe-based systems have shown promising selectivity, but the development of an industrially-viable solid is hindered by the limited understanding of structural and electronic performance descriptors in such complex materials as well as the scarce solubility among the two metals. In this contribution, the synthesis of a set of catalysts featuring distinct carbonaceous carriers and metals ratios through different preparation routes and their in-depth characterization enables to uncover the impact of proximity and particle size of Cu and Fe (Figure 1).<sup>2</sup> In addition, the role of potassium as a promoter is investigated. The kinetic footprints of the reaction are elucidated in detail, allowing the determination of activation energies that rationalize the high selectivity to higher alcohols. Lastly, the stability of the best performer was assessed for 100 h on stream.



**Figure 1** Parameters varied in the investigation of CuFe-based catalysts for higher alcohols synthesis.

[1] H.T. Luk, C. Mondelli, D. Curulla-Ferré, J.A. Stewart, J. Pérez-Ramírez, *Chem. Soc. Rev.*, **2017**, 46, 1358.

[2] H.T. Luk, C. Mondelli, S. Mitchell, S. Siol, J.A. Stewart, D. Curulla-Ferré, J. Pérez-Ramírez, submitted.

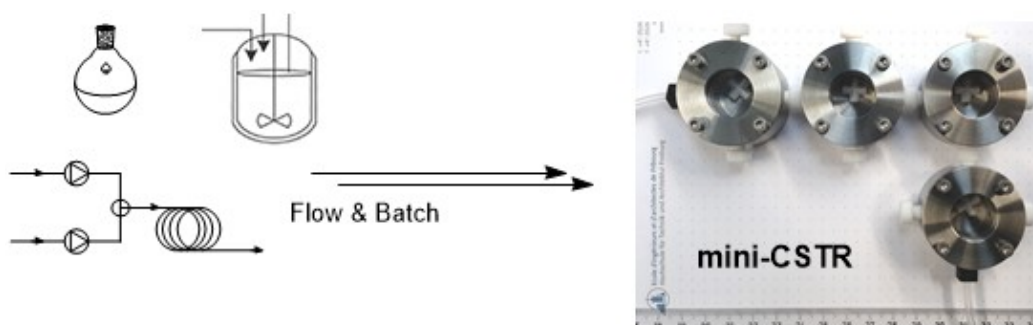


## Miniaturized Continuous Stirred-tank Reactors - mini-CSTR, a New Process Tool for the Lab

R. Marti<sup>1</sup>, E. Vanoli<sup>1</sup>, M. Kaehr<sup>1</sup>

<sup>1</sup>HES-SO Haute école spécialisée de Suisse occidentale, Haute école d'ingénierie et d'architecture Fribourg, Institute ChemTech

Process intensification, continuous processing and the quest for state-of-the-art and new process tools are the driver for innovation in chemical production. We developed a simple in-house prototype of a miniaturized continuous stirred-tank reactor (mini-CSTR) based on the work by Jensen. The big advantage of this mini-CSTR equipment is that it is possible working with "slow" reaction as well as with suspensions in a continuous mode.



Here, we present our work, which consists in manufacturing and assembling of the mini-CSTR in different designs and materials. The use of this equipment in typical reactions, like the Henry nitro aldol reaction or Grignard reaction, and its comparison and critical discussion with the reactions in batch conditions and micro reactors. And finally, preliminary scale-up runs and costs evaluations of the new mini-CSTRs.

Jensen *et al.*, *React. Chem. Eng.*, **2016**, *1*, 501-507.

## Selective oxidation of methane to methanol by isolated copper site(s) on oxide supports

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<sup>1</sup>ETH Zürich, <sup>2</sup>Shell, <sup>3</sup>Paul Scherrer Institute

The vast amount of methane, the difficulty associated with its transportation and its major impact on global warming makes the conversion of methane to a transportable liquid product a very important goal. In that context, the direct conversion of methane to methanol is very attractive, but remains one of the grand challenges in chemistry and catalysis. For the past two decades, metallozeolites, in particular those based on Cu, have emerged as a promising class of materials able to directly convert methane to methanol.<sup>[1]</sup> However, further development has been impeded by the lack of information regarding the structure of the active sites, a key for rational design and development. Surface Organometallic Chemistry (SOMC) has emerged as a powerful approach to generate so-called well-defined heterogeneous catalysts amiable to structure - activity relationship. SOMC is particularly useful to generate metal sites with controlled oxidation state and nuclearity through the selective grafting of tailored metal complexes followed by a thermal treatment of the material to remove organic ligands.<sup>[2]</sup>

Here will be described the synthesis and characterization of isolated copper site(s) supported on oxidic materials, with a fine control of the nuclearity and oxidation state of the copper centers. Material produced using this strategy display high selectivity and productivity of methanol per copper center, when appropriate - tailored - Cu precursors and oxide supports are used. A detailed discussion on the key parameters will be provided.

[1] A. van Bokhoven et al. *Angewandte Chemie International Edition* **2016**, 55, 5467.

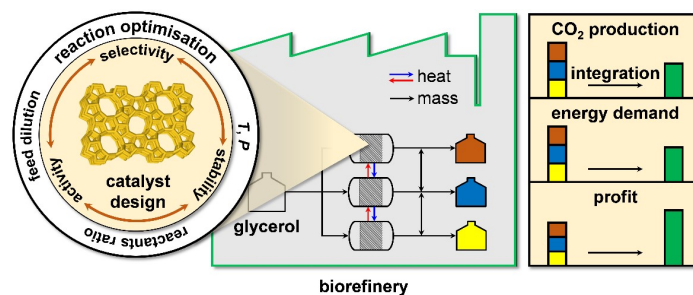
[2] Copéret et al. *Chem. Rev.* **2016**, 116, 323-421.

## Techno-economic assessment of a glycerol biorefinery

C. Mondelli<sup>1</sup>, G. M. Lari<sup>1</sup>, G. Pastore<sup>1</sup>, M. Haus<sup>1</sup>, Y. Ding<sup>2</sup>, S. D'Angelo<sup>1</sup>, A. Dall'Ara<sup>1</sup>, S. Papadokonstantakis<sup>2</sup>, J. Pérez-Ramírez<sup>1\*</sup>

<sup>1</sup>ETH Zurich, <sup>2</sup>Chalmers University

Glycerol conversion into chemicals is pursued to valorise a burgeoning byproduct in the bioenergy sector. Although heterogeneous catalysts enabling efficient and green transformations have been developed, the evaluation of the environmental and economic footprint that would be associated with their large-scale application has often been neglected, limiting their commercial attractiveness. Furthermore, the impact of integrating different glycerol upgrading routes within a biorefinery, which is highly instrumental to determine the effective sustainability and profitability of biodiesel production, has not been assessed. Here, processes to manufacture of the most relevant derivatives of glycerol (lactic acid, acrylic acid, glycerol carbonate, propanediols, epichlorohydrin, and allyl alcohol) are rigorously modelled and assessed by life-cycle analysis based on the performances of the state-of-the-art catalysts.<sup>1</sup> The results indicate that they are more attractive than the conventional technologies nowadays applied for the production of the same chemicals and highlight limited catalyst selectivity and stability, high boiling point of the solvent, and high dilution as the process variables mostly contributing to the environmental and cost metrics. Combination of the processes simulating a prospective glycerol biorefinery is estimated to decrease CO<sub>2</sub> emissions and energy requirements by 15 and 32%, respectively, and increase profit by 5% if the glycerol feed is split equally among all routes. To minimise the ecological impact of the biorefinery, glycerol should be rather divided in an 80:20 mass ratio among 1,2-propanediol and glycerol carbonate production.<sup>1</sup> In order to strengthen the significance of this innovative approach, which holds potential to guide both fundamental chemical research and process design in the development of CO<sub>2</sub>- and other biorefineries, the impact of capital costs is being determined on the basis of the expected market volumes of the starting material and the target products.



**Figure 1** Illustration of the concept of a glycerol biorefinery and of the economic and environmental advantages as compared to separated upgrading processes.

[1] G.M. Lari, G. Pastore, M. Haus, Y. Ding, S. Papadokonstantakis, C. Mondelli, J. Pérez-Ramírez, *Energy Environ. Sci.*, doi:10.1039/C7EE03116E.

## Investigation of a possible Mars-van Krevelen mechanism of the aqueous ethanol oxidation

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The gold-catalysed oxidation of aqueous bioethanol provides an alternative for production of chemicals in an environmentally friendly manner.<sup>[1]</sup> However, little is known about the reaction mechanism and the catalytic sites of ethanol and oxygen. In the case of carbon monoxide oxidation over Au/CeO<sub>2</sub> a Mars-van Krevelen mechanism has been experimentally identified.<sup>[2]</sup> Our research aims to understand the reaction mechanism and the adsorption sites, in order to identify how to optimize the catalyst. Our studies show that the reaction mechanism depends on the choice of the support. Figure 1 shows the reaction order dependency of 1%Au over three different supports, identifying a reaction order of zero, 0.5 and 0.7, for TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZnO, respectively. The order is directly correlated with the reducibility of the support. Our catalytic results are associated with in situ X-ray adsorption spectroscopy at the Au L<sub>3</sub> edge, which allowed us to identify the absence of oxygen adsorption on the gold surface. The combining results suggest that aqueous ethanol oxidation follows the Mars-van Krevelen reaction mechanism, when catalysed by gold supported on reducible oxides. Hereafter, the reducibility of the support during reaction conditions will be evaluated by X-ray spectroscopy techniques.

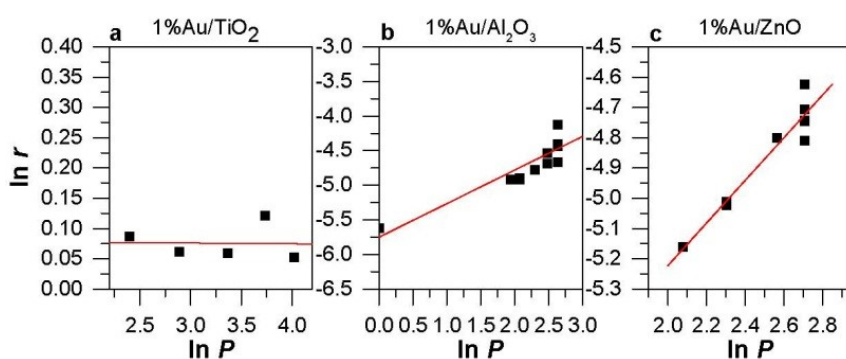


Figure 1. Oxygen dependency of the reaction over gold nanoparticles supported on titania (a), alumina (b), and zinc oxide (c).

[1] C. H. Christensen, B. Jørgensen, J. Rass-Hansen, et al., *Angew. Chemie - Int. Ed.* **2006**, *45*, 4648–4651.

[2] M. Lohrenscheit, C. Hess, *ChemCatChem* **2016**, *8*, 523–526.

**Surface modified CeO<sub>2</sub> nanoparticles supported on electrospun nanofibers: an effective photocatalyst in the visible and the UV**

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In this work, the photocatalytic oxidation of Azorubine under visible and UV light irradiation using a CeO<sub>2</sub> nanocomposite is reported. Environmentally friendly nanofiber mats from pullulan and polyvinyl alcohol were fabricated with electrospinning technique and they were used as the support for CeO<sub>2</sub> nanoparticles. CeO<sub>2</sub> deposition was optimized to overcome the significant negative effect of nanoparticle agglomeration on photocatalytic activity. Subsequently, modification of immobilized CeO<sub>2</sub> nanoparticles was done using generation 3 of poly (amidoamine) dendrimer. The structure and morphology of the synthesized nanocomposite were characterized using FTIR, SEM, and TGA. We find a significant improvement in photocatalytic activity of the CeO<sub>2</sub> nanocomposite in decolorization of Azorubine under visible light compared to both CeO<sub>2</sub> and TiO<sub>2</sub> nanoparticles benchmark. Photocatalytic conversion was strongly pH dependent and in acidic pH, 100 % of dye was removed in visible light exposure due to a simultaneous adsorption process. Generated electrons and holes as well as hydroxyl radicals, singlet molecular oxygen, and super oxide radical anions were shown to be active in the photo oxidation mechanism. The CeO<sub>2</sub> nanocomposite was stable during the photocatalytic process and it was reusable in multiple photocatalytic cycles.

**Time-Resolved Spectroscopic Study of NH<sub>3</sub>-SCR on Cu/SSZ-13**

R. G. Nuguid<sup>1,2</sup>, A. Marberger<sup>1,2</sup>, A. Petrov<sup>1,3</sup>, A. Clark<sup>1</sup>, P. Steiger<sup>1,2</sup>, M. Elsener<sup>1</sup>, O. Kröcher<sup>1,2</sup>, M. Nachtegaal<sup>1</sup>, D. Ferri<sup>1\*</sup>

<sup>1</sup>Paul Scherrer Institut, <sup>2</sup>École polytechnique fédérale de Lausanne, <sup>3</sup>ETH Zürich

Catalysts often operate under highly dynamic reaction conditions, for example when temperature and gas feed composition vary with time. Understanding the catalytic mechanism under these transient conditions is a crucial step to develop new catalytic systems or optimize existing ones. A particularly dynamic catalytic reaction is the selective catalytic reduction (SCR) of NO by NH<sub>3</sub> used to control emissions from automobile diesel exhaust gas streams. A copper-exchanged small pore size zeolite (Cu/SSZ-13) has emerged as a commercial option for its high NO conversion at low temperature and high hydrothermal stability [1]. Here, we used *operando* X-ray absorption spectroscopy (XAS) with sub-second time resolution to obtain unprecedented molecular insights into the reaction mechanism at relevant process conditions [2].

In a typical *operando* experiment, 1000 ppm of NO or NH<sub>3</sub> was fed together with 6 vol% O<sub>2</sub> and 2 vol% H<sub>2</sub>O to Cu/SSZ-13 at 190, 225 and 270 °C. At time zero either NO or NH<sub>3</sub> was switched on. The gas composition after the catalyst bed was monitored continuously by MS, while the structural changes associated with the catalyst were followed with time-resolved quick XAS at a time resolution of 0.5 s. The large XAS data set was analyzed using principal component analysis confirming the presence of 3-4 main components. This approach enabled to obtain novel findings that are critically important to develop the working model of the Cu/SSZ-13 SCR catalysts. In the case of NO addition to the NH<sub>3</sub>/H<sub>2</sub>O/O<sub>2</sub> flow, the existence of 75% of Cu(I) species at 190°C indicated that the oxidation of Cu(I) to Cu(II) is the rate limiting step in this temperature regime for this low loaded (ca. 1.4 wt% Cu) Cu/SSZ-13 catalyst. In the case of the NH<sub>3</sub> cut-off from the SCR feed, an NH<sub>3</sub> inhibition effect on the re-oxidation of Cu(I) was observed. Moreover, a fourfold coordinated Cu(II) species was identified as the reaction intermediate during relaxation of the inhibition, which was previously proposed by theoretical calculations. Finally, Cu-nitrate species appeared only when NH<sub>3</sub> was depleted to low levels, thus away from SCR conditions.

This approach was complemented by identical diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) that provide information on the nature of the adsorbates. This work shows that transient experiments represent a powerful approach to obtain detailed mechanistic insights of catalytic reactions.

[1] Andrew M. Beale, Feng Gao, Ines Lezcano-Gonzalez, Charles H.F. Peden, Janos Szanyi, *Chem. Soc. Rev.*, **2015**, 44, 7371-7405.

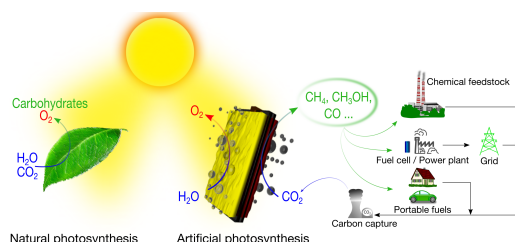
[2] Adrian Marberger, Andrey W. Petrov, Patrick Steiger, Martin Elsener, Oliver Kröcher, Maarten Nachtegaal, Davide Ferri, *Nat. Catal.*, **2018**, 1, 221-227.

## Development of Robust Photocathodes for Solar Induced CO<sub>2</sub> Reduction

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<sup>1</sup>Laboratory for Molecular Engineering of Optoelectr

Due to the intermittency of most renewable energy sources, development of efficient storage techniques particularly in the form of chemical fuels has gained increasing interest in the past decades. Hydrogen has long been considered as the main solar chemical fuel<sup>[1]</sup> but CO<sub>2</sub> based fuels have drawn considerable attention in the last years because of the variety of chemicals that can be produced.



CO<sub>2</sub> reduction can yield different chemical products but it corresponds to a major drawback for industrial application. Indeed, control of the reduction products is challenging, due to close thermodynamic potential of the different redox couples. Additionally, large overpotentials are required to achieve reasonable performances due to the high chemical stability of CO<sub>2</sub> molecules. Because of these drawbacks, there is a need for new efficient catalysts or photocatalysts.<sup>[1]</sup> In this work, the development of robust photocathodes for CO<sub>2</sub> photoreduction has been investigated. Copper Iron oxide in its delafossite crystalline structure has been shown to own adequate energetic bands, to be stable under operating conditions and to absorb a large portion of the solar spectrum.

Unfortunately, experimental photoelectrochemical performances are currently low compared to the theoretical one, computed from the absorption spectrum.<sup>[2]</sup> This low activity is likely originated from surface trap states, which favour interfacial recombination losses. We introduce different strategies in order to passivate the trap states and enhance charge transfer. On one hand, surface treatments such as the utilization of overlayers and catalysts are investigated. On the other hand, bulk engineering has also been used to modify the material's composition and structure, and thus alter the density of surface states at the semiconductor-liquid interface.

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## Understanding lignin fast pyrolysis using model compounds

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Lignocellulosic biomasses can be considered as important feedstocks for chemicals, fuels and energy. They are mainly composed of cellulose, hemicellulose and lignin. Lignin is an amorphous and highly branched polymer of *p*-coumaryl, coniferyl, and sinapyl alcohols [1]. Its unique structure makes it a potential source of a wide variety of fuels and chemicals, particularly aromatic compounds [2].

Fast pyrolysis is one of the most promising methods for lignin conversion [3]. An understanding of the reaction mechanisms involved is of vital importance to improve pyrolysis performance and to optimize the yield to specific products. In this regard, pyrolysis of model compounds containing linkages that resemble those presented in lignin provide insight into the deconstruction of this polymer [4,5].

A study of model compounds with  $\beta$ -O-4 linkages presented in lignins as well as characteristic  $\alpha$ - and  $\gamma$ -hydroxyl groups is proposed. Fast pyrolysis processes carried out using a tandem pyrolysis reactor coupled to a gas chromatograph-mass spectrometer (py-GC/MS) of (3,4-dimethoxyphenyl)methanol; 1-(3,4-dimethoxyphenyl)propane-1,2,3-triol and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol is intended. Using this information, reaction pathways of the model compounds will be proposed to achieve a better understanding of the depolymerization of the polymer structure as a whole.

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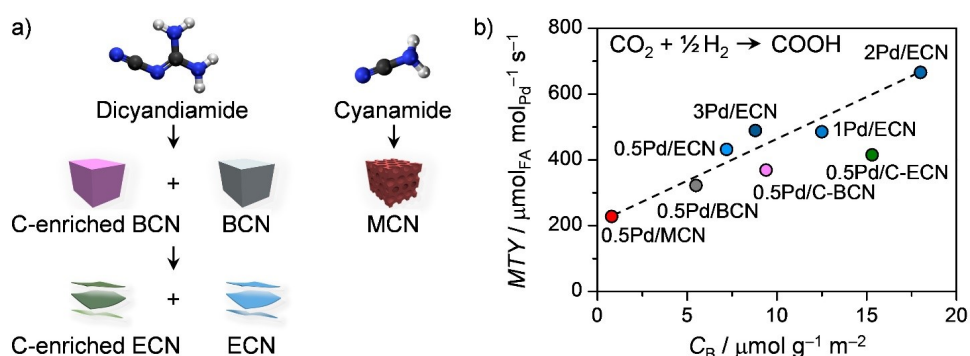


## Enhanced base-free formic acid production from CO<sub>2</sub> over Pd/g-C<sub>3</sub>N<sub>4</sub> by tuning of the carrier defects

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The development of cost-effective and sustainable catalytic technologies to transform CO<sub>2</sub> into chemicals is essential to reduce the environmental impact of fossil fuels. Its hydrogenation to formic acid (FA) is attractive in view of avoiding the substantial ecological implications of the production of syngas currently used as a feedstock for the manufacture of this commodity and potential energy vector.<sup>1</sup> Here, we initially evaluated a series of bifunctional catalysts comprising metals supported on bulk graphitic carbon nitride (BCN) in CO<sub>2</sub> hydrogenation to FA without additional base, identifying Pd as the best performer. Enhanced FA production was attained by careful tuning of the edge-defects of the carrier, where amino groups are available for CO<sub>2</sub> activation,<sup>2</sup> and of the size and distribution of the Pd nanoparticles, required to split H<sub>2</sub>. Concerning the support, a boost in the defect content was approached exploring bottom-up synthesis methods, *i.e.* soft-templating (MCN) and carbon enrichment (C-BCN) upon polymerization, and top-down strategies, *i.e.* thermal exfoliation of the as-prepared solid (ECN) (Figure 1a). The nature and density of these sites was assessed by temperature-programmed desorption of CO<sub>2</sub>, infrared spectroscopy upon CO<sub>2</sub> adsorption at the reaction pressure, and <sup>15</sup>N solid state nuclear magnetic resonance spectroscopy. The highest productivity stemmed from the sample featuring the strongest basicity and abundant and not excessively agglomerated Pd particles (Figure 1b). Selection of adequate temperature, pressure, and reaction time further improved the performance, reaching an 18-times higher turnover frequency compared to the best analogous material used in base-free FA formation from CO<sub>2</sub>.<sup>3</sup>



**Figure 1** a) Synthetic approaches to tailor the morphology of the g-C<sub>3</sub>N<sub>4</sub> carrier. b) Dependence of the metal time yield (MTY) of FA over supported Pd catalysts on the concentration of basic sites (C<sub>B</sub>).

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## Zeolite-based heterogeneous catalysts for the selective oxidation of methane to methyl trifluoroacetate

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The conversion of methane to useful chemicals is a difficult yet intriguing and rewarding task as it has the potential to eliminate the prevalent natural gas flaring by providing novel routes to its valorisation. In this context, the direct selective oxidation of methane to methanol receives significant attention from the scientific and industrial community alike. The facile over-oxidation of methanol in conditions that activate methane impedes the 'direct methane to methanol' (DMTM) processes from reaching high yields.<sup>[1]</sup> The derivatization of methanol to esters such as methyl trifluoroacetate and methyl bisulfate renders high yields possible but nearly all catalytic processes reported for this chemistry so far, employ homogeneous catalysts.<sup>[2]</sup>

In this work, we show the possibility to use zeolites as heterogeneous catalysts for the oxidation of methane with hydrogen peroxide to yield methyl trifluoroacetate. Commercial mordenite catalyzes the conversion of methane to oxygenates, which include methyl trifluoroacetate, formic acid and carbon dioxide. The loading of copper onto mordenite dramatically increases the selectivity to the ester (> 90% at 6% methane conversion). Such an effect has been related to the ability of Cu<sup>2+</sup> to scavenge OH<sup>°</sup> radicals that are usually responsible for the deep oxidation of primary oxygenates.<sup>[3]</sup> Thus, copper acts as a selectivity modulator but is not the active site as the introduction of copper does not translate in an increase in oxygenates produced. The activity of commercial zeolites to oxidize methane in water with hydrogen peroxide has previously been assigned to the presence of iron impurities in commercial zeolites.<sup>[3]</sup> However, in our experiments with trifluoroacetic acid, loading of iron onto mordenite did not result in an increase in activity. On the contrary, we postulate Lewis-acidic, framework-associated aluminum to be the active site, given that such a species has been reported for its ability to activate both, hydrogen peroxide and alkanes.<sup>[4]</sup>

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**Combining in situ powder XRD and ex situ quenching experiments to optimize cobalt spinel water oxidation catalysts**

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Artificial photosynthesis is an important chemical transformation for harvesting renewable energy by using sunlight to split water into oxygen and hydrogen, which can be further converted into chemical fuels. Technological challenges in water oxidation revolve around the half reaction involving a complex four electron transfer process, which remains the main challenge for catalyst development. Therefore, current research on the design and construction of cost-effective, stable and efficient water oxidation catalysts (WOCs) is becoming increasingly relevant for widespread catalytic application. In this respect, robust and low-cost spinel-type  $\text{Co}_3\text{O}_4$  is a highly promising candidate to replace gold-standards Ir, Ru, and Pt-containing WOCs. However, while the catalytic performance of  $\text{Co}_3\text{O}_4$  is well-known it is still challenging to control its catalytic parameters associated with oxidation states, morphology, crystallinity, defects, and surface area.

In this study, we combine in situ powder X-ray diffraction (PXRD) and quenching investigations of typical lab-scale hydrothermal  $\text{Co}_3\text{O}_4$  synthesis. The kinetic data obtained by the in situ PXRD measurements were evaluated using *Gualtieri* and *Sharp-Hancock* approaches. For reaction temperatures over 185 °C a change of the growth mechanism is clearly demonstrated by both models. Quenching experiments provided valuable information about the effect of amorphous cobalt-containing phases on the catalytic activity. We show that combining ex situ investigations with an in situ technique offers valuable insights for the optimization of parameter-sensitive hydrothermal synthesis of essential energy materials.

## Development of Heterogeneous Catalysts for Alkane Dehydrogenation from Surface Organometallic Chemistry Principles

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A shift from oil-based naphtha cracking to shale-based ethane cracking has created an imbalance in the production and demand of propylene.[1,2] This has resulted in strong demands for alternative light olefin production routes. While on-demand propane dehydrogenation is practiced industrially, the current industrial catalysts suffer from fast deactivation and require frequent regeneration.[1,3] In attempts to deconvolve specific factors which effect catalyst stability and selectivity, and ultimately design more effective catalytic systems, we have prepared several well-defined catalysts using Surface Organometallic Chemistry.[4] This involves a two-step approach where molecular precursors are first grafted to the surface of an oxide support followed by either a thermolysis or reduction step. This contribution will present structural characterization of these heterogeneous systems and their activity in the dehydrogenation of alkanes.

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## Engineered Pd embedded N, S co-doped graphene wrapped magnetic core-shell nanospheres: as a highly stable catalyst for the Suzuki-Miyaura coupling reaction

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Pd-catalyzed Suzuki cross-coupling has played an important role for selective construction of C-C bonds and mainstay of modern synthetic organic chemistry for the producing of biaryl compounds. Clever introduction of core/shell magnetic materials into graphene can combine the high adsorption ability of graphene with the separation convenience of magnetic nanoparticles. Graphene is an electron-rich, hydrophobic nano-planar structures with high delocalized  $\pi$ -electron system. The  $\pi$ - $\pi$  stacking of the graphene nanosheet and the aromatic substrates of the Suzuki coupling reaction make the reactant more accessible toward the active sites of the Pd NPs, which accelerates the coupling reaction. Moreover, the lone pair electrons in N and S dopants led to the generation of negative charge on the surface of graphene that not only induce anchoring sites for high dispersion and strong interactions of Pd NPs on the surface of graphene sheets, but also modulate electronic property of graphene, therefore directly affect on the activity and the stability of Pd NPs on the support during the coupling reaction. Based on these premises, the engineered nitrogen and sulfur co-doped graphene wrapped magnetic core-shell supported Pd nanoparticles were synthesized through main following steps. Firstly,  $\text{Fe}_3\text{O}_4$  was prepared and then coated with silica to increase its stability against aggregation and oxidation. Secondly, prepared magnetic core-shell was functionalized with amine groups to create a positive charge for enhance the interaction of the  $\text{Fe}_3\text{O}_4@SiO_2$  with graphene oxide and then wrapped with graphene to enhance adsorption of aromatic substrates on the surface of catalysts through  $\pi$ - $\pi$  stacking. Thirdly, graphene was doped with N and S to increase the grafting of Pd in hybrid. Finally, Pd species were anchored on the surface of the pre-engineered structure to produce  $\text{Fe}_3\text{O}_4@SiO_2@N, S\text{-wG}@Pd$ . The resulting exhibited high performance in Suzuki reaction and biaryls were obtained in high yields that can be attributed to efficient  $\pi$ - $\pi$  interactions between aromatic reactants and catalyst. Moreover, the incorporation of N and S into graphene led to high anchoring and well-dispersion of Pd NPs on the nanocomposite surface offering large amounts of active centers that strongly increase the interaction between Pd and substrates to decrease Pd leaching. Additionally, magnetic property of the  $\text{Fe}_3\text{O}_4$  nanoparticles was efficient to easy separation of catalyst and therefore improve its reusability.

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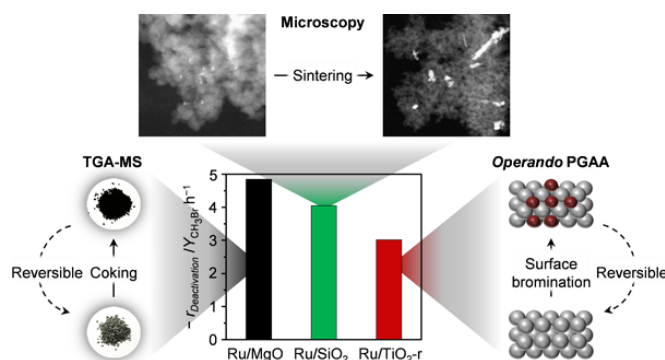
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## Deactivation mechanisms of ruthenium-based catalysts in the hydrodebromination of dibromomethane

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Bromine-mediated upgrading of methane is a promising technology, targeting the transformation to methyl bromide as a platform chemical analogous to methanol, for the manufacture of readily transportable commodities. However, the practical relevance of this process is contingent on the reforming of dibromomethane (DBM), the main byproduct formed in the methane halogenation step.<sup>1</sup> Catalytic hydrodebromination, involving halogen elimination by hydrogen addition, comprises an attractive route to the desired CH<sub>3</sub>Br. Silica-supported ruthenium was demonstrated as a selective catalyst for DBM hydrodebromination ( $\leq 87\%$  to CH<sub>3</sub>Br), however no conclusions on stability were provided.<sup>2</sup> In this study, we show that ruthenium catalysts deactivate independent of the preparation method or nature of the support. Bromination, sintering, and fouling are identified as the main deactivation mechanisms leading to dramatic activity losses (**Figure 1**). Ru-catalysts based on supports with a strong basic or acidic nature suffer from rapid deactivation primarily due to carbon deposition. In contrast, catalysts mainly affected by bromination preserved their initial performance better. In this regard, Ru/TiO<sub>2</sub>-r exhibited improved performance than the Ru nanoparticles on TiO<sub>2</sub>-a, owing to the higher dispersion of Ru as a surface layer over the support, indicating that the active phase morphology affects the poisoning process. Coking and bromination are reversible deactivation mechanisms, unlike sintering, which is pronounced for the Ru/SiO<sub>2</sub> catalyst due to the weaker ruthenium-support interaction. These findings constitute a basis towards the design of superior hydrodebromination catalysts and demonstrate the critical need for further research in this field.



**Figure 1** Extent and type of deactivation in three ruthenium-based catalysts after exposure to reaction conditions for 20 hours with main characterization techniques used for this study.

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## In Vivo Metathesis of Artificial Metalloenzymes: Progress Towards Non-Natural Metabolism

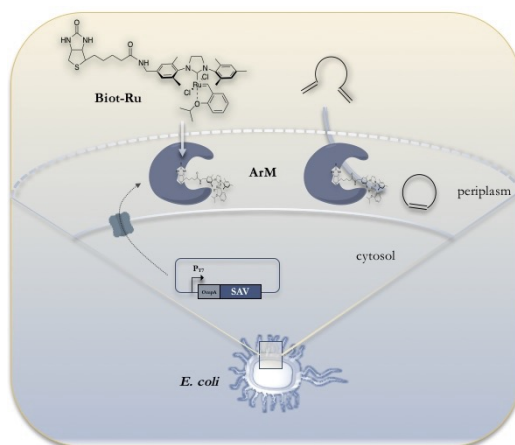
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Biocatalysis is a continuously evolving field with applications in the pharmaceutical and agrochemical industries. Genetic engineering tools allow to enhance biological systems by engineering new-to-nature reactions. To perform such reactions, artificial metalloenzymes (ArM) represent a versatile tool resulting from the incorporation of organometallic moieties within a protein scaffold. Artificial metalloenzymes based on the biotin-streptavidin technology have been shown to enable bioorthogonal reactions and their chemogenetic optimisation.

A recent report in our group led to the development of a ruthenium-based artificial metalloenzyme evolved by directed evolution that catalyzes ring closing metathesis in the periplasm of *Escherichia Coli* [1]. This suggests the possibility to perform *in vivo* non-natural reactions, paving the way for innovative applications in metabolic engineering.

Herein, we describe a "metathase-dependent" system based on a biotinylated Hoveyda-Grubbs catalyst, aiming to introduce non-natural substrates which can be readily converted in metabolic precursors upon ring closing metathesis. Metathesis reactions have no equivalent in nature, therefore allowing to bypass biochemical pathways and allow cell survival in engineered *E. coli* cells lacking specific metabolic routes.



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## Unravelling metal-ligand combination effects for the hydrogenation of carbon dioxide using molecular volcano plots

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Converting carbon dioxide to valuable compounds, such as formic acid and methanol, is a promising route towards decreasing its atmospheric concentration. The hydrogenation of carbon dioxide to formate is particularly attractive due to its important use as a platform chemical in several fabric dyeing processes. However, the catalysts that accelerate this reaction have principally been developed by trial and error; guidelines on how best to tune the catalysts are lacking. Here, we apply molecular volcano plots to uncover novel metal-pincer catalysts for the hydrogenation of carbon dioxide to formate. The creation of linear free energy scaling relationships and molecular volcano plot from a combination of six metals (Fe, Ru, Os, Co, Rh, and Ir) and seven tridentate pincer-type ligands revealed several complexes near the volcano top, suggesting that these species are promising catalysts. The activity of  $d^6$  metal-based catalysts (Fe, Ru, and Os), which lie slightly on the strong binding (left) side of the volcano, can be improved when combined with electron-withdrawing ligands.  $d^7$  based catalysts (Co, Rh, and Ir), on the other hand, are best paired with electron-donating ligands. The identification of ideal metal/ligand combinations should greatly aid in obtaining maximum efficiency for this catalytic reaction.



**Integrated Chemical Systems for the On-chip Synthesis of Compound Libraries**

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Efficient synthesis of diverse compound libraries that are used in drug discovery and other fields is a challenging venture. A “molecular factory” that is compiled of interlinked reaction sites, separated from each other with in- and outlets for compounds to enter and leave a microreactor, has great potential to optimise the workflow of library synthesis. Our work aims at an on-chip system on which a multitude of compounds can be synthesised in a single operation by cascaded catalytically triggered conversions of a common substrate without the need of intermediate isolation and use of protection group strategies. Key for providing various catalyst sequences is a site-selective deposition of catalysts and a reliable control over individual reaction conditions in a reaction compartment. This large parameter space and the use of telescoped reactions permit the creation of libraries of highly diverse small molecules.

## Effect of Active Sites Structure on Activity of Copper Mordenite in Aerobic and Anaerobic Conversion of Methane to Methanol

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Direct conversion of methane to methanol is an industrially very important process, as it provides a sustainable route from an abundant and clean component of natural gas to one of the main precursors for chemicals synthesis.<sup>[1]</sup> A promising aerobic stepwise process over copper-exchanged zeolites has been suggested; however, a detailed understanding of the mechanism of such a zeolite-catalyzed conversion is still missing.<sup>[2]</sup> We have recently<sup>[3]</sup> proposed an alternative solution to the above problem by showing that selective anaerobic oxidation of methane is possible, where water can be used both to provide oxygen to regenerate the zeolite active centers. However, the intrinsic activity of copper species of different size is still a subject of debate. Furthermore, recent reports suggest the possibility of formation of a mixture of active sites.

Herein we demonstrate the influence of Si/Al ratio of the zeolite mordenite on the possible configurations of the active copper oxo sites, and therefore on the activity of the material in the process of aerobic and anaerobic conversion of methane into methanol. We show that the samples with high Si/Al ratio preferentially contain isolated copper cations, while the samples with low Si/Al exhibit the mixture of copper monomers and oligomers. Using infrared spectroscopy of absorbed nitrogen monoxide and hydrogen as well as the X-ray absorption spectroscopy we have established the spectroscopic signatures for monomeric and oligomeric copper oxo sites. We show that the samples containing preferentially monomeric copper cations demonstrate higher methanol yield per mol of copper and selectivity. Such reactivity comes at a price of a poor activity in the water reactivation reaction, preventing these sites from stabilizing and releasing molecular hydrogen while oxidizing Cu(I) into Cu(II). The samples with lower Si/Al ratios, on the other hand, both provide sufficient methanol yield and facilitate an energetically less costly release of hydrogen, thus offering optimal conditions for the efficient selective direct methane conversion without oxygen.

This difference is most probably associated with the stabilization effect of the water molecules interacting with active copper sites. Altogether, these data can serve as a basis for the further improvement of existing and design of novel materials for direct conversion of methane into methanol.

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## Development of a microfluidics assay for the genetic evolution of artificial metalloenzymes

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Incorporation of a transition metal catalyst within a protein scaffold enables the formation of artificial metalloenzymes (ArMs) with non-natural reactivities.<sup>[1]</sup> The catalytic activity and selectivity of such systems can be optimized by either chemical optimization of the metal cofactor or genetic evolution of the host protein. Integration of the biotinylated ruthenium complex [CpRu(Biot-Quinoline)(H<sub>2</sub>O)]<sup>[2]</sup> into the binding pocket of streptavidin (Sav) affords an artificial deallylase capable of uncaging a protected coumarin yielding a fluorescent readout.<sup>[3]</sup> Herein, we present a microfluidics-based high-throughput assay<sup>[4]</sup> to evolve the catalytic activity of an artificial deallylase. Single *E. coli* cells with surface-displayed Sav are encapsulated in droplets together with the protected coumarin substrate and the biotinylated cofactor. The catalytically active mutants can be sorted by fluorescence-assisted cell sorting (FACS) and the identified hits can be subjected to a further round of optimization. This method can be applied to evolve various ArMs *in vivo* and enable the screening of large libraries in an iterative and straightforward manner.

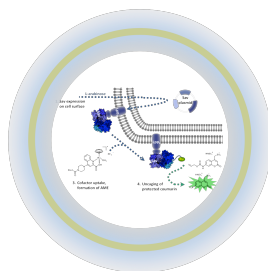


Figure 1: Schematic representation of a microfluidics approach to evolve the activity of an artificial de-allylase based on the biotin-streptavidin technology

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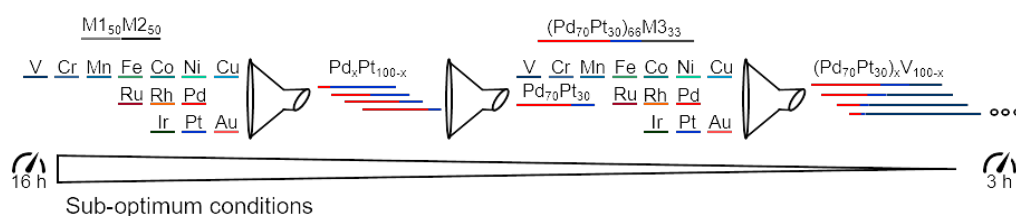
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## A Multi-Metallic Catalysts Screening Method Applied to the Hydrogenolysis of Diphenyl Ether Revealed a Highly Active Catalyst for the Valorization of Lignin

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The valorization of lignin, an aromatic polymer present in biomass, is crucial to the development of commercially viable biorefineries. To do so, the discovery of efficient catalysts that cleave aryl ether bonds is essential. Among them, bimetallic catalysts exhibit high efficiencies, but have not been studied in a systematic way. Therefore, we developed a method to screen multi-metallic catalysts using a model substrate (diphenyl ether). We found that nanoparticles composed of 70 % of palladium and 30 % of platinum could quantitatively cleave diphenyl ether at 95 °C and atmospheric pressure of hydrogen. In addition, the nanoparticles are selective towards phenol partial hydrogenation into cyclohexanone. This research provides insight into the activity of multi-metallic catalysts towards hydrogenolysis of diphenyl ether.



Schematic of the screening procedure: sub-optimum conditions are maintained while the catalysts gain in efficiency. The colors in the bars represent the metal in each catalyst. The length of each bar represent the different molar ratio in each catalyst.

**Metal/Metal Oxide Hybrid Nanocrystals As Electrocatalysts For CO<sub>2</sub> Reduction Reaction**S. B. Varandili<sup>1</sup>, R. Buonsanti<sup>1\*</sup><sup>1</sup>Department of Chemical Science and Engineering, EPFL Valais Wallis, 1951 Sion, Switzerland

Recent years have seen a remarkable growing international interest in CO<sub>2</sub> capture and sequestration to promote renewable energies in order to avoid a global catastrophe. Among the available methods for CO<sub>2</sub> conversion, electrochemical route is of a promising significance, because of the double advantage of CO<sub>2</sub> utilization as well as storage of renewable energies <sup>1</sup>. Nevertheless, there are challenges, limiting the practical implementation of electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub> RR), including: large overpotentials and low selectivity towards multicarbon products. Copper still remains the only suitable electrocatalyst to produce C<sub>2</sub>/C<sub>3</sub> products, yet it is not active and selective enough <sup>2</sup>.

In the current work, Cu/metal oxide hybrid nanocrystals are proposed and investigated as novel catalysts to attain a superior performance for electrochemical CO<sub>2</sub> RR. The idea is to exploit the complementary properties of copper/metal oxides to facilitate the CO<sub>2</sub> adsorption and the stabilization of oxygen-containing intermediates identified as reaction limiting step in the transformation of CO<sub>2</sub> into hydrocarbons <sup>3</sup>. Colloidal seeded-growth approach was employed to access this material combination in a tunable manner so to uncover univocal relations between the structure and the catalytic behavior. The study on the synthesis parameters indicated that surfactants, reaction temperature and [Cu precursor]/[seed] ratio play a crucial role in the formation of high-yield hetero-dimers. Moreover, we indicated that the construction of the Cu/CeO<sub>2</sub> interface could noticeably boost the selectivity towards CO<sub>2</sub> RR products and particularly ethylene. These results promise a new potential approach toward the design of efficient electrocatalysts for CO<sub>2</sub> RR.

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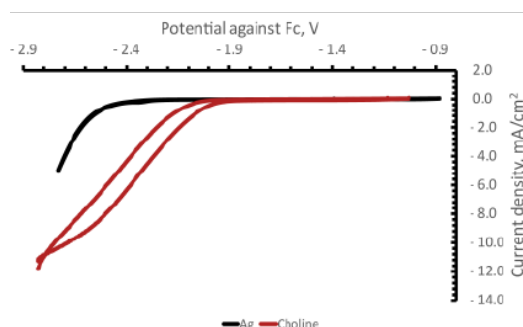
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**Choline-based systems for electrochemical reduction of carbon dioxide**D. Vasilyev<sup>1</sup>, A. V. Rudnev<sup>2</sup>, P. Broekmann<sup>3\*</sup>, P. J. Dyson<sup>4\*</sup>

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Carbon dioxide is a cheap and abundant C1 stock, therefore methods for its valorization are of high interest<sup>[1,2]</sup>. Electrochemical reduction of CO<sub>2</sub> allows to obtain a wide range of products<sup>[3]</sup>, which along with the possibility to employ renewable sources of energy makes it an attractive way to convert carbon dioxide. Ionic liquids were shown to significantly decrease the reduction onset potential and to suppress parasitic hydrogen evolution reaction<sup>[4]</sup>. Later synergistic effect of hydroxyl substituent and the activity of the ionic liquid cation was demonstrated<sup>[5]</sup>.

Herein, we demonstrate activity of choline-based systems for co-catalysis of CO<sub>2</sub> reduction on silver electrode. Choline-based systems significantly decrease onset potential for the carbon dioxide transformation, which makes them a promising alternative to ionic liquid-based systems due to its low cost. Further improvements of the systems employing the deep eutectic solvent (DES) concept is under investigation.



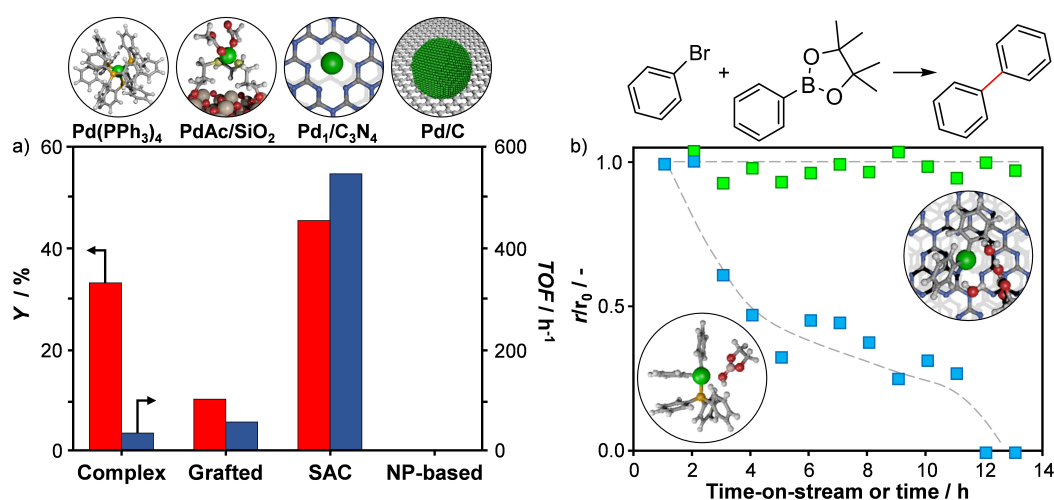
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## A heterogeneous single-atom palladium catalyst surpassing homogeneous systems for Suzuki coupling

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Palladium-catalyzed cross-couplings, central tools in fine-chemical synthesis, predominantly employ soluble metal complexes despite recognized challenges with product purification and catalyst reusability. Attempts to tether these homogeneous catalysts on insoluble carriers have been thwarted by suboptimal stability. The application of supported Pd nanoparticles has faced limitations due to insufficient activity under the mild conditions needed to avoid thermal degradation of the substrates or products. Single-atom heterogeneous catalysts lie at the frontier.<sup>1</sup> Here, we show that the Pd atoms anchored on exfoliated carbon nitride capture the advantages of both worlds, comprising a solid catalyst that matches the high chemoselectivity and broad functional group tolerance of established homogeneous catalysts for Suzuki couplings, while demonstrating robust stability in flow (Figure 1).<sup>2</sup> The adaptive coordination environment within the macroheterocycles of carbon nitride facilitates each catalytic step. The findings illustrate the exciting opportunities presented by nanostructuring single atoms in solid hosts for catalytic processes that remain difficult to heterogenize.



**Figure 1** a) Comparative performance with state-of-the-art catalysts in terms of yield (red bars) and turnover frequency (TOF, blue bars). b) stability test over the single atom (green) and Pd(PPh<sub>3</sub>)<sub>4</sub> (blue) catalysts.

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**Selectivity control during the one-pot conversion of aliphatic carboxylic acids to linear olefins through tandem hydrogenation/dehydration**J. Yeap<sup>1</sup>, B. Rozmysłowicz<sup>1</sup>, J. Luterbacher<sup>1\*</sup><sup>1</sup>EPF Lausanne

Olefins are important building blocks for the synthesis of higher value chemicals in the petrochemical industry and they are typically produced from fossil fuels. As an alternative to fossil fuel-based chemicals, biomass-derived carboxylic acids could serve as a viable replacement feed for olefin production. However, the production of olefins from carboxylic acids in one step remains a challenge due to the stability of carboxylic acids and the tendency of olefins to over-hydrogenate during hydrogenation, leading to alkanes.

In the present study, we have studied the one-pot catalytic conversion of linear aliphatic carboxylic acids to linear olefins via tandem hydrogenation/dehydration reactions. Hexanoic acid was converted to a mixture of hexenes over Cu nanoparticles supported on commercial silica-alumina (Siral 70) in a continuous flow reactor. At 483 K and 5 bar H<sub>2</sub> gauge pressure, we obtained 98.5% conversion of hexanoic acid, with a molar product distribution of 88.9% hexenes and 11.1% hexane. Remarkably, we observed a brusque selectivity switch to 99.9% hexane at 100% conversion.

A product intermediates study shows that when switching from a feed of pure hexene to a mixture of hexene and hexanoic acid, overhydrogenation of hexene can be suppressed. In addition, hexene temperature-programmed desorption (TPD) and FT-IR spectroscopy reveals that adsorption of hexanoic acid prevents hexene from accessing the catalyst surface, thus avoiding overhydrogenation. Reactions using butyric acid as feed also exhibit similar phenomena. We have also performed reactions utilizing butyric acid derived from biomass fermentation, albeit with significant catalyst deactivation.

We propose that the presence of a small amount of carboxylic acid on the surface of the catalyst prevents overhydrogenation of the olefins. In light of these results, current efforts are targeted at applying this concept to explain similar phenomena in other reactions, particularly in biomass conversion. The presence of numerous carboxyl groups in native/pre-treated biomass might explain the difference in catalyst performance/selectivity when processing model feed versus real biomass. Furthermore, the addition of carboxylic acids to the reaction medium during biomass upgrading could afford more control over the selectivity of the reaction.



**Self-templated formation of  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  hollow spheres for enhanced electrocatalytic water oxidation**Y. Zhao<sup>1</sup>, G. R. Patzke<sup>1\*</sup><sup>1</sup>University of Zurich, Department of Chemistry

Low dimensional nanosized subunits (nanoparticles, nanosheets and nanorods), offer high surface area and active sites for efficient electrocatalytic water splitting while could largely reduce the ion transport pathways and promote electronic conductivity.<sup>[1]</sup> The three-dimensional micro-sized hollow structures, on the other hand, usually provided robust chemical stability, thus preventing the possible aggregation of active materials during the water reduction (hydrogen evolution reaction HER) or oxidation (oxygen evolution reaction OER) process.<sup>[2]</sup> Therefore, the employment of complex micro/nano structures can address problems related to nano-unstability or micro-low surface area for water splitting. Transition metal oxides, especially cobalt oxides  $\text{Co}_3\text{O}_4$ , have attracted increased attention for OER under alkaline conditions due to its high conductivity and earth abundance. Herein, we report a simple approach to synthesize  $\text{Co}_3\text{O}_4$  hollow spheres-type structures without introduced template. Co-spheres precursors were formed during the solvothermal process, then the following nonequilibrium heating treatment process could easily convert to  $\text{Co}_3\text{O}_4$  core-in-double-shell hollow structure with preserved as prepared morphology. Furthermore, we synthesized a series of  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  hollow spheres and show that due to synergistic effects the  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  hollow spheres show high active sites, surface area and could be highly efficient electrocatalysts during OER process.

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## Smart Hydrogenated Wrinkled Yolk@Shell Architecture of TiO<sub>2</sub> toward Powerful Visible Light Photocatalytic Application

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Semiconductor photocatalysts have attracted increased attention due to their great potential for solving energy and environmental problems. Among them TiO<sub>2</sub> has received broad attention as a favorable candidate for use in water splitting, dye-sensitized solar cells and photocatalysis reactions in recent years due to its outstanding chemical and physical properties. Several TiO<sub>2</sub> morphologies have been extensively investigated including nanotubes, nanowires, hollow spheres, core@shell and yolk@shell architectures. Yolk@shell architectures have attracted particular attention and emerged as a modern generation of smart functional structures. But, the development of stable and highly active visible light absorption titania photocatalysts still remains a significant challenge. Therefore, the preparation of reduced TiO<sub>2</sub> nanomaterials containing Ti<sup>3+</sup> species has been considered as a promising environmentally friendly strategy to enhance visible light photoactivity. Based on these premises, herein we report the preparation of an unprecedented yolk/shell wrinkled TiO<sub>2</sub> architecture with excelling photocatalytic activities under visible light irradiation. This method includes solvothermal, partial etching and hydrogen treatment sequential preparation steps. The solvothermal step lead to yolk@shell TiO<sub>2</sub> (Y@S-TiO<sub>2</sub>) structures which can generate a multi reflection of incident light so as to promote an efficient light harvesting due to an enhanced surface area and light scattering ability based on the hydrothermal alkaline partial etching. The hydrogen treatment process generated Ti<sup>3+</sup> species on the surface of TiO<sub>2</sub> which facilitate electron-hole separation, decreasing the band gap of titania to visible region. The resultant yolk@hydrogenated wrinkled shell TiO<sub>2</sub> architecture exhibited a high efficiency in visible light oxidation of alcohols to the corresponding aldehydes (up to 90 in conversion, 97% in selectivity).

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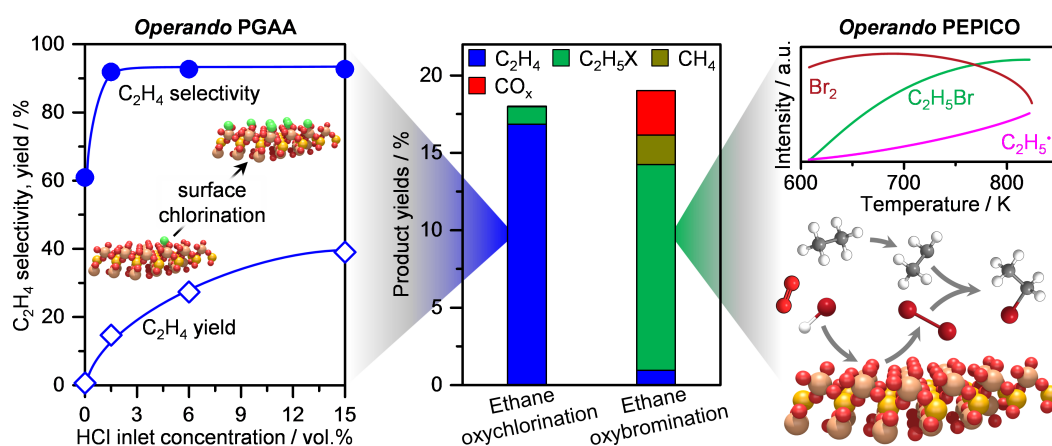
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## Mechanistic origin of the halogen-dependent selectivity switch in catalyzed alkane oxyhalogenation

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Catalytic alkane oxyhalogenation, comprising the reaction of an alkane with O<sub>2</sub> and hydrogen halide (HX, X = Cl or HBr) has been recently demonstrated as a promising strategy for the functionalization of natural gas into light olefins and/or alkyl halides, both key building blocks for the manufacture of chemicals, polymers, and pharmaceuticals. Although several systems were shown to be efficient catalysts (e.g. iron phosphate, europium oxyhalide, titanium dioxide),<sup>1,2</sup> there is still no clear understanding on the mechanism of this reaction. In this study, we couple *operando* prompt gamma activation analysis (PGAA) to determine the amount of surface halogen species on iron phosphate (FePO<sub>4</sub>), as well as *operando* photoelectron photoion coincidence (PEPICO) spectroscopy to quantify the presence of radical species under reaction conditions (Figure 1). This is combined with steady-state kinetic tests and Density Functional Theory calculations that rationalized the observed favored olefin production (selectivity ≥ 95%) in oxychlorination and the preferred generation of alkyl bromides (selectivity ≤ 95%) in oxybromination (Figure 1). In particular, although both reactions undergo alkyl halide generation and consecutive dehydrohalogenation steps, it was found that alkane activation occurs primarily on the catalyst surface in oxychlorination, while it follows a radical-chain mechanism in the gas phase with the Br<sub>2</sub> produced *in situ* during oxybromination, originating the observed selectivity differences (Figure 1).



**Figure 1** Unraveling the reaction pathways involved in ethane oxychlorination (left) and oxybromination (right) over FePO<sub>4</sub> leading to the observed selectivity patterns (middle).

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## Thermally Conductive Micro-structured Catalysts for Process Intensification

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Although it is widely recognized that spatially structured catalysts/reactors are at the heart of process intensification, the engineering of the heat management in structured reactors has not received great attention until recently [1]. There is potential, however, for significant enhancement of radial heat transfer rates in technical multitubular packed-bed catalytic reactors with external cooling if the random packings of catalyst pellets are replaced by structured catalysts with thermally connected, highly conductive substrates. This presentation will review related work from our group, addressing two different technologies for alternative enhanced catalyst supports, namely conductive honeycomb monoliths [2–10] versus conductive open-cell foams [11–14], and exploring in particular their application to syngas chemistry processes [9,10, 15–17]. The new concept of “packed foams” will be also reported [18–20]. The results point out that conductive structured catalysts are particularly advantageous in compact reactors with short tubes, due to their flow-independent conductive heat transfer mechanism [21]. This offers unique potential for compact GtL reactors in applications e.g. on off-shore platforms and FPSOs.

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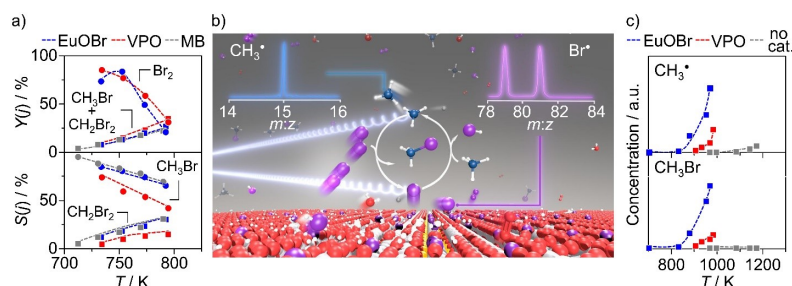
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## Evidence of radical chemistry in catalytic methane oxybromination

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Understanding the mechanism of the heterogeneously-catalyzed functionalization of methane and other light alkanes present in natural gas is more than a scientific curiosity, as it may unlock an efficient conversion of this increasingly abundant, relatively cheap, and potentially renewable feedstock into commodities.<sup>1,2</sup> Here, the mechanism of catalytic methane oxybromination to bromomethane (CH<sub>3</sub>Br) and dibromomethane (CH<sub>2</sub>Br<sub>2</sub>), highly attractive platform molecules, was studied over benchmark vanadyl pyrophosphate ((VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, VPO) and europium oxybromide (EuOBr) catalysts.<sup>2-4</sup> The kinetic fingerprints of the reaction, such as its temperature onset, the product distribution, the apparent reaction order with respect to methane, and the apparent activation energy, are found to be very similar to those of non-catalytic gas-phase bromination, which is known to involve methane activation *via* radical intermediates (Figure 1a). *Operando* photoelectron photoion coincidence (PEPICO) spectroscopy is introduced as a powerful technique to detect the evolution of gaseous methyl (CH<sub>3</sub><sup>•</sup>) and bromine (Br<sup>•</sup>) radicals over the oxybromination catalysts (Figure 1b). The data hint a strong correlation between the production of CH<sub>3</sub>Br and the concentration of CH<sub>3</sub><sup>•</sup> (Figure 1c). Overall, the findings suggest a mechanism comprising the surface-catalyzed generation of Br<sup>•</sup> and bromine (Br<sub>2</sub>) followed by gas-phase methane bromination (Figure 1b), which is rationalized by Density Functional Theory calculations. Uncovering the role of surface and gas-phase steps in halogen-mediated C-H bond activation over heterogeneous catalysts has important implications for the prospective design of catalytic and reactor systems for methane valorization *via* oxybromination chemistry.



**Figure 1** a) Yield and selectivity data of methane oxybromination over EuOBr and VPO and non-catalytic methane bromination (MB). b) Detection of radicals in methane oxybromination by *operando* PEPICO spectroscopy and proposed reaction scheme. c) Relative concentrations of CH<sub>3</sub><sup>•</sup> and CH<sub>3</sub>Br in methane oxybromination over EuOBr and VPO and in the absence of a catalyst.

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## Time-resolved XAS studies on ethylene oxidation over Cu-Pd-exchanged Y zeolite catalysts

J. Imbao<sup>1,2</sup>, M. Nachtegaal<sup>1\*</sup>, J. A. van Bokhoven<sup>1,2\*</sup>

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The Wacker process is one of the most efficient organic synthetic methods for manufacturing aldehydes and ketones. This liquid-phase homogeneous catalytic process, however, suffers from the difficulty in the separation of the products from the catalyst solution; high corrosivity associated with HCl excess; and the formation of undesired chlorinated byproducts [1]. Thus, many studies were devoted to designing a heterogeneous chloride-free solid-vapor Wacker catalyst system to potentially overcome these problems. However, most of these catalyst systems either lacked sufficient activity or stability due to inefficient reoxidation of palladium so it is the aim of this study to gain a deeper understanding of the reaction mechanism of heterogeneous Wacker process to develop and engineer better catalysts. In this talk, first direct evidence of electron transfer between zero-valent palladium and bivalent copper under catalytic conditions during heterogeneous Wacker oxidation will be presented which was revealed by means of transient XAS experiments coupled with kinetics studies.

Heterogeneous Wacker catalysts were prepared by ion exchange of Pd(II) and Cu(II) on zeolite Y because it is closely similar to the homogeneous system and it is one of the most active and stable catalysts for heterogeneous Wacker oxidation [2]. Time-resolved XAS measurements [3], with a resolution of 0.5 s, were performed at the Cu and Pd K-edges in transmission mode in a quartz capillary reactor cell connected to a mass spectrometer in steady-state and transient conditions wherein the partial pressure of a reactant is changed to monitor structural and oxidation state changes in the catalyst in different kinetic regimes.

A reaction order of zero was determined for O<sub>2</sub>, which is similar to the homogeneous process. The reaction order became half order at much lower O<sub>2</sub> partial pressures. Under standard (O<sub>2</sub>-rich, zero-order) steady-state conditions, it is difficult to observe the presence of Cu(I) species because its reoxidation to Cu(II) is favored. Transient experiments were conducted where the time-resolved variations of the fractions of Pd and Cu species from the linear combination fits of their respective XAS spectra showed that lowering the partial pressure of O<sub>2</sub> in the reactant feed led to the partial reduction of Cu(II) to Cu(I); and Pd(II) to Pd(0). Increasing the partial pressure of oxygen again in the reactant feed led to the reoxidation of Pd(0) to Pd(II) and Cu(I) to Cu(II). Without detecting the transient presence of Cu(0) and Pd(I), our results suggest that a one-electron transfer from two Cu(II) ions to reoxidize Pd(0) to Pd(II) is at work in this heterogeneous Wacker catalyst. This is corroborated by an optimum Cu/Pd  $\geq 2$  in an active heterogeneous Wacker catalyst.

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**CO<sub>2</sub> to methanol mechanism investigation over Cu/ZnO based catalysts by operando time-resolved XAS and SSITKA-FTIR studies**

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Catalytic transformation of CO<sub>2</sub> into liquid fuels (primarily methanol) has received great attention during previous decades due to increased global energy demand and the need to decrease of carbon emissions to the environment. Despite numerous studies, the development of an appropriate heterogeneous catalyst that will actively and selectively convert mixtures of CO<sub>2</sub> and H<sub>2</sub> to methanol continues to be a “Holy Grail” in catalysis and chemical engineering. The most investigated catalyst formulations in CO<sub>2</sub> to methanol hydrogenation are copper-zinc-based materials, which are widely used for syngas transformation to methanol. Several research groups claimed, that either metallic Cu steps decorated with Zn atoms, a synergy of Cu and ZnO at the interface or a surface Cu/Zn alloy are required for the system to work. The reason why the mechanism of CO<sub>2</sub> hydrogenation as well as the nature of the catalytic site are still the subject of intense debate, can be explained by the fact that conclusions in previous studies were based either on *ex-situ* and computational techniques or by using *in situ* techniques at conditions, which were far away from the real catalytic experiment (15-30 bars; 260 °C). We aimed to bridge this gap by performing *in situ* and *operando* characterization at relevant pressures.

For this reason nanosized Cu/ZnO catalysts encapsulated into a zeolite matrix were synthesized. During catalyst design, attention was focused on maintaining a high dispersion and intimate contact between Cu and ZnO phases to achieve the highest possible number of active sites and consequently highest activity. This material as well as commercial CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts were examined by a variety of relevant characterization techniques in order to determine their morphological and surface properties. In particular, attention was given to *in situ* and *operando* spectroscopic techniques (XAS and FTIR) that were utilized to both optimize catalyst surface properties and investigate in detail the reaction mechanism. During SSITKA-FTIR investigation at 15 bars it was found that formates are primary products, labile and undergo full interconversion during the isotope switch. At the same time surface methoxy species, formed only at high H<sub>2</sub> pressure, are secondary products for Cu/Zn/zeolite catalyst and do not undergo isotope exchange, and are most probably spectators. Results of *operando* XANES study provided an evidence of involvement of the Cu and ZnO interface in catalytic cycle of CO<sub>2</sub> hydrogenation to methanol.

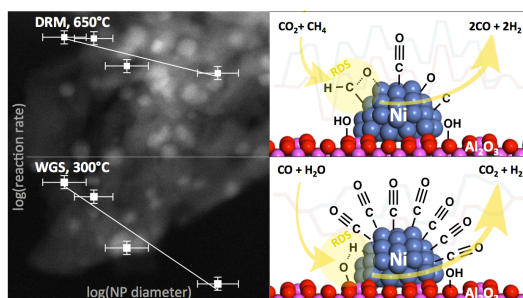


## The Role of Ni/Al<sub>2</sub>O<sub>3</sub> Interfaces in Water-Gas Shift and Dry Reforming Elucidated by Multi-scale First Principles Modeling

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The reactivity of metal nanoparticles (NPs) catalysts is often affected by the nature of the support, which can in some instances be ascribed to the formation of NP/support interface sites that take part in catalysis. The interface effect is commonly rationalized based on stronger reactants adsorption or their facile activation on such sites compared to bare NPs, as indicated by Density Functional Theory (DFT) evaluation of potential energy surfaces (PES). [1,2] However, the relevance of these steps to the overall reaction rate depends on the preferred reaction pathways at reaction conditions, which usually cannot be inferred based solely on PESs. Hereby,[3] we combine a multi-scale DFT/mean field micro-kinetic modeling approach with the experimental evaluation of the activity of Al<sub>2</sub>O<sub>3</sub>-supported Ni NP catalysts (2–16 nm) to investigate the reactivity of the Ni/Al<sub>2</sub>O<sub>3</sub> interface towards the water-gas shift (WGS) and the dry reforming of methane (DRM), two key industrial reactions with common elementary steps and intermediates but held at significantly different temperatures: 300 vs 650 °C, respectively. Our study reveals that the metal/support interface is the most active site for WGS because the NP is covered with CO under reaction conditions and reactive hydroxyl groups can only be stabilized at the interface. Conversely, DRM is not affected by the interface since the NP surface is available for catalysis at higher temperatures.



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## Chemical Reactions by High-resolution Neutron Imaging

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Despite the obvious scientific link between mesoscopic structure of a catalyst and the catalytic performance, its rational design remains a challenge due to lack of true dynamic information. Recording non-periodic, dynamic processes of technical catalysts with high spatial and temporal resolution on the mesoscopic scale is a particular challenge. In addition to these challenges, the probing beam must be compatible to the harsh reaction conditions (e.g., gas environment of the sample and temperature) [1]. Our approach is based on the interaction of neutrons with matter, which is highly isotope selective. The interaction of neutrons with many types of materials is relatively weak, and thus, for example, the neutron beams can easily penetrate relatively thick aluminum walls of a chemical reactor. At the same time, neutrons have a large cross-section with hydrogen, i.e., we can follow the change in hydrogen concentration by means of neutron imaging of an operating chemical reactor [2].

We demonstrate the feasibility of the operando technique based on time-resolved high resolution neutron imaging by mapping the water concentration distribution inside catalysts beads during sorption enhanced CO<sub>2</sub> methanation reaction at ambient pressure and temperatures up to 300°C with a spatial and temporal resolution of 50 μm and 60 s, respectively. We find that the diffusion of water through catalysts is a critical reaction constraint. We derive the Thiele parameter [3,4] of a technical catalyst as a quantitative measure supporting the materials and reactor design of sorption enhanced methanation. Water accumulation as an indicator for reaction kinetics is specific to the sorption enhanced CO<sub>2</sub> methanation reaction, and as such not easily applicable to other catalytic systems. For these systems, we introduce a combination of neutron microscopy with Steady State Isotopic Transient Kinetic Analysis (SSITKA), in which the isotope labelling (hydrogen/deuterium exchange) is followed by neutron imaging and infrared spectroscopy.

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## Oxidative Dehydrogenation of Ethane over MoVNbTe-Oxide Catalysts: On the Way to a Commercial Process

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The crystalline M1 phase of MoVTenb mixed oxide (Fig.1) has proven to be an excellent catalyst for the oxidative dehydrogenation (ODH) of ethane [1]. These catalysts have been first patented by Mitsubishi for the ODH [2]. Catalysts with very high M1-phase purity were reported by hydrothermal synthesis from soluble metal salts, followed by high temperature treatment under nitrogen [3]. These MoVTenb mixed oxides are known to lose tellurium under high temperature treatment and during the catalytic reaction [4]. Even more important, the soluble precursor  $\text{Te}(\text{OH})_6$  is commercially not available in larger scales. All these issues have been strong hurdles for a commercialization of an ODH-process based on this type of catalyst until now.

In the first step of our research, a stoichiometry of the mixed oxide was identified to be superior in ODH having a high V- and a low Te content ( $\text{Mo}_1\text{V}_{0.3}\text{Nb}_{0.1}\text{Te}_{0.1}$ ) [5]. In the next step, a new synthesis route was developed based only on metal oxides using chelating oxoligands in the hydrothermal crystallization. Surprisingly, this method leads to M1-phase without the necessity of high temperature treatments, and hence to a much more active catalyst. This new synthesis method further allowed a M1-phase with even less niobium and tellurium and with even higher activity (Fig. 2). The combined intense catalyst as well as process development increased the ethylene productivity almost by a factor of 4. This catalyst/process is now going to be further optimized in a pilot plant.

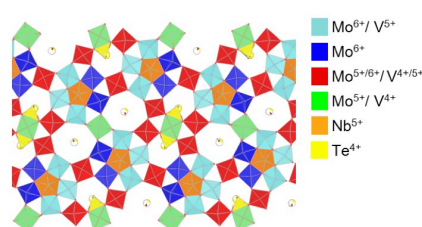


Fig. 1 M1-Crystal structure

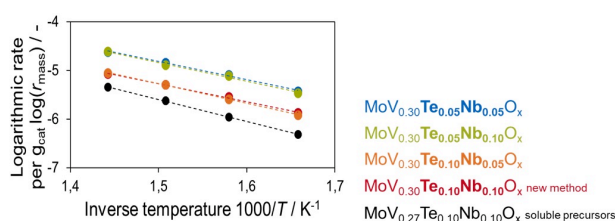


Fig. 2 Activity of different catalyst generations

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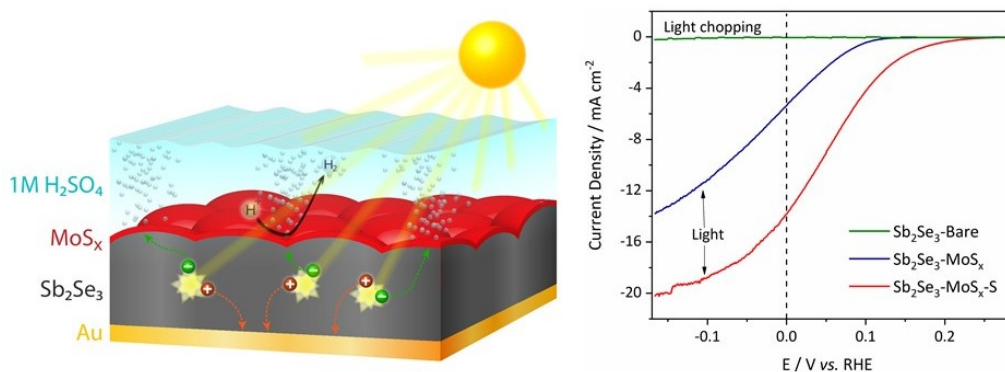
[5] D. Melzer et al., *Angew. Chem. Int. Ed.*, **2016**, 55, 8873 -8877 (supplemental material)

## Photocorrosion-resistant $\text{Sb}_2\text{Se}_3$ photocathodes with earth abundant $\text{MoS}_x$ hydrogen evolution catalyst

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The poor stability of high efficiency photoabsorber materials in aqueous media is one factor holding back the realization of photoelectrochemical (PEC) water splitting for large scale, practical solar fuels generation. Here, we demonstrate that highly efficient thin film  $\text{Sb}_2\text{Se}_3$  – fabricated by a simple, low temperature selenization of electrodeposited Sb – is intrinsically stable towards photocorrosion in strongly acidic media (1 M  $\text{H}_2\text{SO}_4$ ). Coupling with a photoelectrodeposited  $\text{MoS}_x$  hydrogen evolution catalyst gives high photocurrents ( $5 \text{ mA cm}^{-2}$  at 0 V vs. RHE) and high stability without protective layers. A low temperature sulfurization of the  $\text{Sb}_2\text{Se}_3$ - $\text{MoS}_x$  stack dramatically improved the onset potential, resulting in high photocurrent densities up to  $\sim 16 \text{ mA cm}^{-2}$  at 0 V vs. RHE. The simplicity with which these photocathodes are fabricated, combined with the high photocurrents and stability, make  $\text{Sb}_2\text{Se}_3$  a strong candidate for scalable PEC cells [1].



**Figure 1.** A highly efficient  $\text{Sb}_2\text{Se}_3$  photocathode (device architecture shown above) is resistant to photocorrosion in strongly acid media without protective overlayers.

[1] R. R. Prabhakar, W. Septina, S. Siol, R. Wick-Joliat, T. Moehl, D. Tilley, *J. Mater. Chem. A*, **2017**, 5, 23139-23145

## In-Operando Potential Sensing at the Semiconductor-Liquid Junction: Exposing the Surface Energetics and Interfacial Kinetics during Photoelectrosynthetic Reactions

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Storing the energy of the sunlight into feedstock chemicals or energy-rich compounds, such as hydrogen, appears as an enticing option to extend the use of solar energy beyond the possibilities of photovoltaics. Among different technologies, photoelectrochemical (PEC) tandem cells for overall water splitting stand out by leveraging their simplicity in design and predicted conversion efficiencies (> 20%).<sup>1</sup> Broadly speaking, this device comprises two photoactive electrodes wired together and in direct contact with water, which upon illumination generate a photovoltage high enough (> 1.23 V) to drive the photoelectrosynthesis of H<sub>2</sub> and O<sub>2</sub> on the surface of the electrodes, so-called photocathode and photoanode, respectively. These complex reactions occur at the semiconductor-liquid junction, and therefore the electrochemical and catalytic properties of this interface, namely the surface potential, overpotential for the reaction, kinetics of charge transfer and recombination... dictate the conversion efficiency. Despite the progress in the last decades, the low performance of photoelectrodes remains a challenge.<sup>2</sup> A better understanding on the electrocatalytic properties of the semiconductor-liquid junction could potentially identify the parameters limiting the overall conversion efficiency opening new avenues to improve the performance.

In recent years, a new group of operando techniques have emerged to bring insightful information on the electrode/electrolyte interface.<sup>3</sup> Here, we present a new technique capable of directly sensing the potential across the semiconductor-liquid junction in combination with a transient photocurrent/photovoltage measurement to probe the surface carrier dynamics (kinetics of photoelectrosynthetic reactions and surface recombination). These results afford, for the first time, direct access to the interfacial information, giving steady-state (interfacial energetics) and transient (interfacial kinetics) electrochemical information in-operando. We believe, these new insights on the dynamics of the semiconductor-liquid junction will potentially unveil the designing principles for a new generation of electrodes with enhanced photoelectrocatalytic properties.

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## Hydrogen Storage - Towards the “Formic Acid Battery”

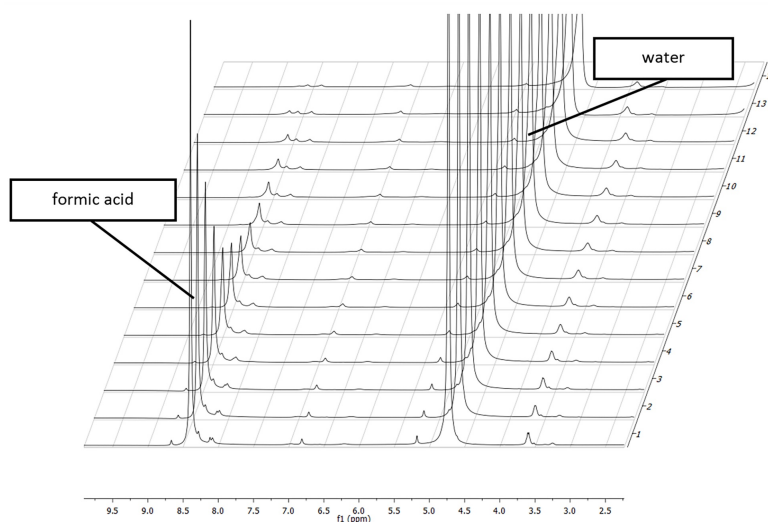
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Hydrogen storage via homogeneously catalyzed carbon dioxide (CO<sub>2</sub>) reduction to formic acid (FA) and the reverse reaction to liberate hydrogen via FA dehydrogenation is a promising technology for a future hydrogen economy.<sup>[1]</sup> Here, we want to highlight vital steps which lead to the development of an FA powered electricity generator (prototype). At the current level of technology, the search for improved catalysts plays a central role.<sup>[2]</sup> Therefore we studied a series of iridium complexes, which are part of a larger group of structures, known to be able catalysts for FA dehydrogenation. Our contribution was the systematic examination of small diamine ligands to evaluate steric and electronic effects.<sup>[3]</sup> The survey included NMR spectroscopic measurements and the determination of the activation energy, E<sub>a</sub>.

In another work, we looked into solvent-FA interactions to elucidate how different solvents and additives stabilize formic acid in case of CO<sub>2</sub> hydrogenation. DMSO<sup>[4]</sup> and water were considered as more relevant solvents and therefore carefully examined. The results are considered as needed tools for engineers to design hydrogen storage devices. The methods we deployed were heat-flow calorimetry, multinuclear NMR -and FTIR spectroscopy as well as computational methods to generate a compressive model of occurring intermediates and species.<sup>[5]</sup> FA dehydrogenation is volunteer reaction despite being endothermic. High-pressure reaction calorimetry revealed to which extent FA dehydrogenation is endothermic under experimental conditions and enabled us to quantify the energy required to dehydrogenate one mole of FA.

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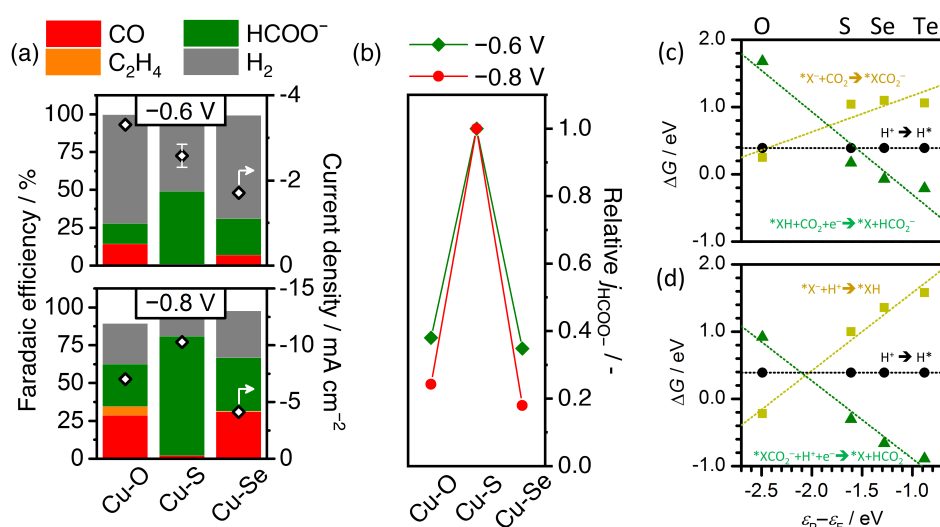
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## Highly selective mechanisms modulated by basicity in chalcogen-modified copper for the electroreduction of carbon dioxide toward formate

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The promising electrocatalytic reduction of carbon dioxide (eCO<sub>2</sub>RR) can potentially become a pillar for sustainability when driven by renewable energy,<sup>1</sup> though its practicality is currently burdened by unsatisfactory catalytic performance. In typically used transition metals, theoretical studies predict suboptimal adsorption energies of intermediates, calling for surface modification strategies.<sup>2</sup> A paradigmatic case is copper, which shows insufficient activity and selectivity control. Nevertheless, sulfur-modified copper (Cu-S) has been recently discovered to favour exclusively HCOO<sup>-</sup> among carbon products, sitting at the top of earth-abundant, cost-effective, and nontoxic electrocatalysts to date.<sup>3</sup> In this contribution, we disclose by combining experimental and theoretical means that basicity impacts the eCO<sub>2</sub>RR in chalcogen-modified copper catalysts (Cu-O, Cu-S, and Cu-Se). More specifically, the peak in selectivity toward HCOO<sup>-</sup> for the Cu-S system in **Fig. 1a-b** is explained by two mechanisms in which the chalcogen plays a fundamental role. The basicity of chalcogen atoms promote both routes, driving the reaction exclusively toward HCOO<sup>-</sup>, **Fig. 1c-d**. These pathways associated to basic sites are potentially applicable to other materials and reactions.



**Figure 1.** (a) Product distribution and (b) relative current density for formate ( $j_{\text{HCOO}^-}$ ) over chalcogen-modified Cu. Key reaction energies as a function of the basicity (c-d). Potentials vs. RHE.

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## Carbohydrate stabilization extends the kinetic limits of chemical polysaccharide depolymerization

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Biomass-derived carbohydrates are important platform molecules for the production of renewable fuels and chemicals. The production of carbohydrates from lignocellulosic biomass requires the extraction of lignin and the cleavage of ether bonds in hemicellulose (mostly xylan) and cellulose chains while minimizing further degradation of the resulting carbohydrates.<sup>1</sup> In inexpensive systems like pure water or dilute acid mixtures, carbohydrate monomer degradation rates exceed hemicellulose and especially cellulose depolymerization rates at most easily accessible temperatures, limiting sugar yields.

Here, we use a reversible stabilization of xylose and glucose by acetal formation with formaldehyde to alter this kinetic paradigm, preventing sugar dehydration to furans and their subsequent degradation (Figure 1). During a harsh organosolv pretreatment in the presence of formaldehyde and low water content, over 90% of xylan in beech wood was recovered as diformylxylose (compared to 16% xylose recovery without formaldehyde). The subsequent depolymerization of cellulose led to carbohydrates yields over 70% and a final concentration of ~5 wt%, whereas the same conditions without formaldehyde led to a yield of 28%.

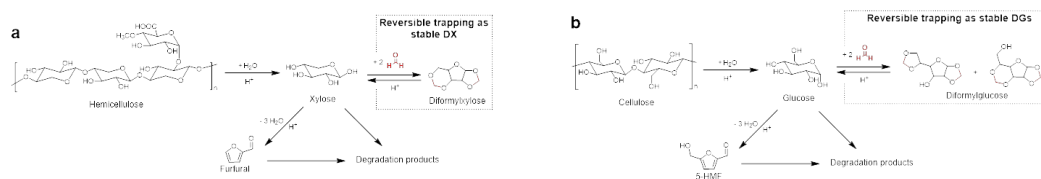


Figure 1. Carbohydrates stabilization by reversibly forming (a) diformylxylose and (b) diformylglucose using formaldehyde during acid-catalyzed biomass pretreatment and cellulose depolymerization, respectively. DX refers to diformylxylose and DGs refers to the two diformylglucose isomers.

This approach could lead to new processes for depolymerizing and valorizing biomass derived-carbohydrates or their stabilized equivalents. For example, when diformylxylose was used as a starting reactant, similar furfural yields (65%) to those obtained with xylose *via* hydrogen transfer (1,2-hydride shift) were achieved without Lewis acid addition. Interestingly, no difference in the reaction kinetics was observed when a Lewis acid was added, which suggested that diformylxylose proceeded to furfural through a new mechanism. In light of these results, current efforts are focused on the utilization of these protected carbohydrates as new platform molecules to produce important building blocks such as furans and polyols.

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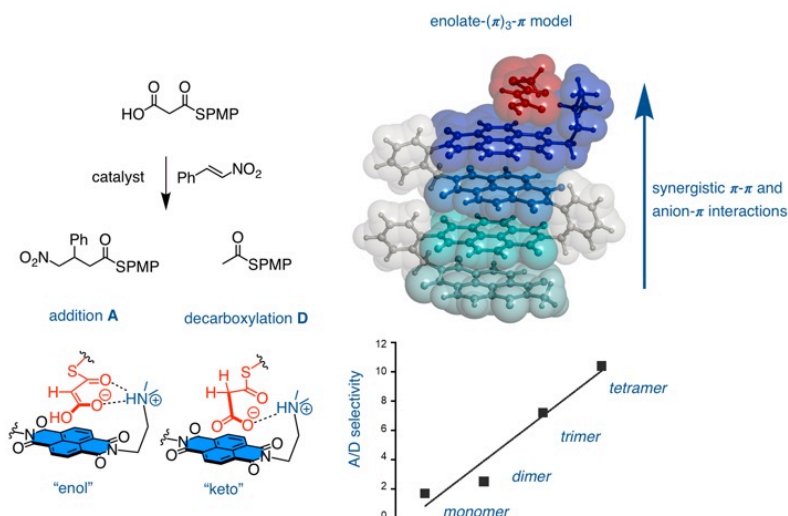


## Synergistic Anion-( $\pi$ )<sub>n</sub>- $\pi$ Catalysis on Covalent NDI Foldamers

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In a conceptually new approach we show that the combination of  $\pi$ - $\pi$  stacking and anion- $\pi$  interactions in  $\pi$ -stacked NDI foldamers reaches so far unreached selectivities in NDI anion- $\pi$  catalysis.<sup>1</sup> A series of up to four covalently bound, face-to-face stacked NDI foldamers was designed and synthesized. To confirm the stacked conformation of the oligomers NMR analysis and UV absorption spectroscopy were performed. Electronic communication within the  $\pi$  stacks could be shown with cyclic voltammetry, steady-state and transient absorption spectroscopy. The reaction of a malonate half thioester with an enolate acceptor is biologically important but intrinsically disfavored and was used to probe the catalytic activity of the oligomers. The chemoselective catalysis increases linearly with the number of NDI units stacked and compared to ratiomeric changes in absorption and decreasing energy of the LUMO levels that show sublinear trends thus results in superlinearity. In computational models the number of NDI units stacked could be correlated to surface potentials, chloride binding energies, and the distances between chloride and  $\pi$  surface and within the  $\pi$  stack. Binding energies of the stacks with “enol” and “keto” reaction intermediates show the preference for planar “keto” tautomers on  $\pi$  acidic surfaces that increases even more with increasing number of NDI units. The experimental results are thus confirmed except for the extraordinary violation of the oligomer’s laws of diminishing returns. Our results show that the existence of anion-( $\pi$ )<sub>n</sub>- $\pi$  interactions together with ongoing investigations on where this linearity stops, promise them a bright future in catalysis and beyond.



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